

PATENT ABSTRACTS OF JAPAN

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(22)Date of filing : 11.03.1992 (72)Inventor : ONO KOJI

(54) SILVER HALIDE PHOTOGRAPHIC SENSITIVE MATERIAL FOR CRT PHOTOGRAPHING

(57)Abstract:

PURPOSE: To obtain a silver halide photographic sensitive material for CRT photographing free from the generation of color remaining property and residual silver even in the case of rapid processing and having high sensitivity, high sharpness and high quality picture.

CONSTITUTION: The silver halide photographic sensitive material has at least one layer of a silver halide emulsion layer and a hydrophilic colloid layer on one side face (A) of a transparent supporting body and at least one layer of a silver halide emulsion layer and a hydrophilic colloid layer, which contains a silver salt of dyestuff and is on the outside of the emulsion layer, on the other side face (B).

LEGAL STATUS

[Date of request for examination]

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[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

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2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

CLAIMS

[Claim(s)]

[Claim 1] Silver halide photosensitive material for CRT photography characterized by having at least one-layer a silver halide emulsion layer and a hydrophilic colloid layer in one field (Ath page) of a transparency base material, and having at least one layer of hydrophilic colloid layers which contained the silver salt of a color outside the silver halide emulsion layer and this emulsion layer in another field (Bth page).

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] About the silver halide photosensitive material which photos this invention and CRT (cathode ray tube) as the light source, it is high sensitivity in detail, and the sharp nature of an image is excellent, and it is related with the silver halide photosensitive material for CRT photography which can be processed quick. [0002]

[Background of the Invention] The silver halide photosensitive material for CRT photography is a film for transparency images as hard copy of CRT images, such as medical-application X-ray CT.

[0003] In recent years, quick processability is increasingly required of sensitive material, and it is not the exception in the sensitive material for CRT.

[0004] In order to lessen for example, the amount of silver halides and to obtain maximum density as one means which raises the processability of sensitive material, forming a silver halide into a granule child etc. is mentioned. However, by this approach, the sharp fall of photosensitivity is caused, and in order to raise the brightness of CRT as a result or to lengthen the exposure time, it is remarkably accompanied by degradation of an image.

[0005] Therefore, in order to obtain desired photosensitivity, the actual condition did not obtain the configuration fake colander which uses a silver halide particle with a large particle size so much unavoidably.

[0006] Consequently, being established became inadequate by quick processing and it had become the cause which the remaining color contamination by residual silver, residual hypo or a coloring matter color, etc. generates.

[0007] Moreover, with having needed the silver halide more than a constant rate inevitably [although there is a film which applied the emulsion only to one side in order to raise the sharp nature of an image as a medical-application sensitive material, in order to maintain high sensitivity and high concentration], consequently having mentioned above, similarly, development nature, fixable, water washability, or drying ability fell, and it had resulted in spoiling the quality of an image that it is easy to generate contamination.

[0008]

[Objects of the Invention] Therefore, even if the purpose of this invention carries out rapid development processing, it is offering the silver halide photosensitive material for CRT photography which there is no generating of remaining color nature and residual silver, and has high definition by high sensitivity and high sharp nature.

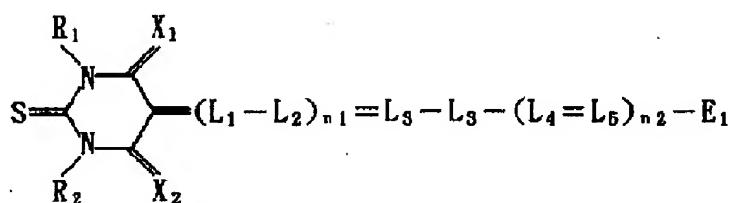
[0009]

[Elements of the Invention] The above-mentioned purpose of this invention is attained by the silver halide photosensitive material for CRT photography which has at least one-layer a silver halide emulsion layer and a hydrophilic colloid layer in one field (Ath page) of a transparency base material, and has at least one layer of hydrophilic colloid layers which contained the silver salt of a color outside the silver halide emulsion layer and this emulsion layer in another field (Bth page).

[0010] Hereafter, this invention is explained in full detail.

- ❖ [0011] When the silver halide photosensitive material concerning this invention is exposed and developed from one transparency base material side (Ath page) and light exposure is the light exposure which gives fogging concentration +1.10 to one field (Ath page), it is 0.10 or less that the concentration of the Bth page is +0.20 or less fogging desirable especially preferably.
[0012] The method of using for the Ath page the approach or color which is the configuration that a Bth page side serves as low sensibility to the exposure from the Ath page, considers as the method of using the emulsion of low sensibility for the Bth page rather than the emulsion of the Ath page or the configuration which makes [many] light absorption at an Ath page side, for example, increases the quantity of the silver content of the Ath page in order to obtain such photograph engine performance, or the method of using a plate-like particle for the Ath page be learned.
[0013] In the silver halide photosensitive material of this invention, many things of the amount of transmitted lights of the light which penetrates a base material and reaches to a low sensibility side in the case of the one side exposure from a high sensitivity side (crossover light) are more desirable than the usual double-sided sensitive material for roentgenography.
[0014] In practical skill, 12% - 75% or less of range has the desirable permeability of the luminescence brightness light of CRT to be used, and it is 65% or less 16% or more more preferably. It is for causing degradation of sharp nature, so that the permeability of the reason of the brightness light of CRT increases.
[0015] As for the silver halide photosensitive material of this invention, it is desirable that orthochromatic spectral sensitization is carried out so that it may correspond to yellowish green luminescence of the fluorescent substance used for CRT. The approach currently indicated by JP,63-168642,A as a spectral sensitization method can be used.
[0016] Next, the color used for this invention is explained.
[0017] In the silver halide photosensitive material for CRT photography, in case the light of specific wavelength is made to absorb and a photographic-emulsion layer is passed, reflective dispersion is carried out from a film holder front face, and the scattered light carries out incidence to an emulsion layer again, and forms an imagewise image. This image deteriorates sharp nature remarkably for the so-called dotage image.
[0018] This invention is being in carrying out absorption prevention of this halation light, and preparing a coloring layer in the outside of the silver halide emulsion layer of the Bth page.
[0019] As for a color, it is desirable to satisfy the following conditions because of the above-mentioned purpose of this invention.
[0020] (1) having [a color]-to luminescence field of CRT to be used-absorption (2) color -- a photograph -- it is inactive chemically and decolorizing or dissolution removing having-on photograph property-bad influence (3) color by the processing process, and not leaving coloring contamination to the sensitive material after processing etc. is mentioned.
Since it is spread about the approach of preparing a color layer conventionally, in the silver halide emulsion layer which a color adjoins and the fall of sensibility, contrast, etc. is brought about, the diffusion prevention approach of a color is learned, for example, the approach using the mordant of a macromolecule as an immobilization technology of water soluble dye is learned.
[0021] However, by this approach, it has the fault which the remaining color contamination after processing tends to produce in quick processing [as / all whose processing times are 60 or less seconds like recently].
[0022] The silver salt of the color in this invention points out the silver salt and the silver complex which are formed of the reaction of a color and complex ion, and a color points out the organic compound which has absorption in (380nm - 700nm) of a visible-spectrum region.
[0023] Although the desirable color which can form hereafter the silver salt used in this invention is mentioned, this invention is not limited to these.
[0024] The above-mentioned color can mention the color expressed with following general formula [1]- [5].
[0025]
[Formula 1]

一般式〔1〕

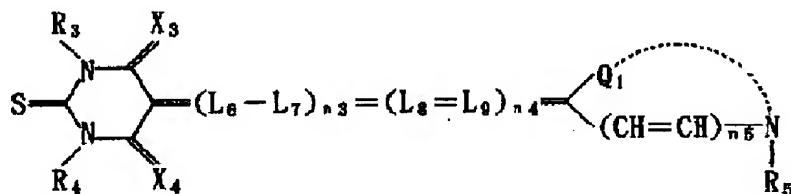


[0026] R1 and R2 express a hydrogen atom, an alkyl group, an alkenyl radical, an aryl group, and a heterocycle radical among a formula, and X1 and X2 express an oxygen atom and a sulfur atom. L1-L5 express a methine group, and n1 and n2 express the integer of 0-2. Moreover, E1 expresses the radical which has an acid nucleus.

[0027]

[Formula 2]

一般式〔2〕

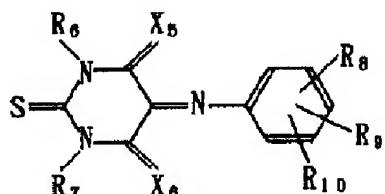


[0028] Among a formula, R3 and R4 are synonymous with R1 and R2 in a general formula [1], and X3 and X4 are synonymous with X1 and X2 in a general formula [6]. L6-L9 express a methine group and n3-n5 express the integer of 0-2. R5 -- an alkyl group and an alkenyl radical -- expressing -- Q1 -- 5 members -- or -- A nonmetal atom group required to form the heterocycle of 6 members is expressed.

[0029]

[Formula 3]

一般式〔3〕

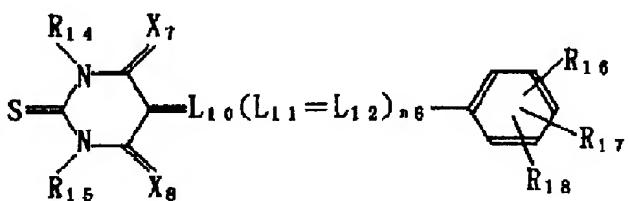


[0030] Among a formula, R6 and R7 are synonymous with R1 and R2 in a general formula [1], and X5 and X6 are synonymous with X1 and X2 in a general formula [1]. R8-R10 A hydrogen atom, an alkyl group, an alkenyl radical, an aryl group, A heterocycle radical, a halogen atom, a cyano group, a sulfonic group, -COR11, -CON(R11)(R12), -N(R11)(R12), -OR11, -SOR11, -SO two R11, -SO2N(R11)(R12), - Expressing N(R11) COR12, -N(R11) SO two R12, -N(R11) CON(R12)(R13), -SR11, and -C OOR11, R11-R13 express a hydrogen atom, an alkyl group, an alkenyl radical, an aryl group, and a heterocycle radical.

[0031]

[Formula 4]

一般式 [4]

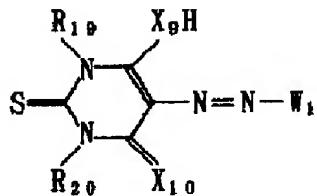


[0032] Among a formula, R14 and R15 are synonymous with R1 and R2 in a general formula [1], and X7 and X8 are synonymous with X1 and X2 in a general formula [1]. L10-L12 express a methine group, and n6 is integer table ** of 0-6. R16-R18 are synonymous with R8-R10 in a general formula [3].

[0033]

[Formula 5]

一般式 [5]



[0034] Among a formula, R19 and R20 are synonymous with R1 and R2 in a general formula [1], and X9 and X10 are synonymous with X1 and X2 in a general formula [1]. W1 expresses an aryl group or a heterocycle radical.

[0035] As an alkyl group expressed with R1-R2 in a general formula [1], a methyl group, an ethyl group, a propyl group, an isopropyl group, n-butyl, tert-butyl, a cyclopentyl group, a cyclohexyl radical, etc. are mentioned, for example. Further these alkyl groups A hydroxy group, a cyano group, a sulfonic group, a carboxyl group, halogen atoms (for example, a fluorine atom, a chlorine atom, a bromine atom, etc.) and an alkoxy group (for example, a methoxy group --) aryloxy groups (for example, a phenoxy group and 4-sulfo phenoxy group --), such as an ethoxy radical aryl groups (for example, a phenyl group --), such as a 2 and 4-disulfo phenoxy group Alkoxy carbonyl groups (for example, a methoxycarbonyl group, an ethoxycarbonyl radical, etc.), such as a 4-sulfophenyl radical, 2, and 5-disulfo phenyl group, and aryloxy carbonyl groups (for example, phenoxy carbonyl group etc.) may permute.

[0036] As for the aryl group expressed with R1 and R2, a phenyl group and a naphthyl group are mentioned. The alkyl group and permutation alkyl group which were expressed with R1 and R2, and the same radical may permute these radicals.

[0037] R1 and R2 As a heterocycle radical expressed, a pyridyl radical, a thiazoline radical, an oxazoline radical, an imidazoline radical, a furil radical, a pyrrolyl radical, a pyrazinyl radical, a pyrimidinyl group, a pilus DAJINIRU radical, the Puri Nils radical, a selenazolyl radical, a sulfo RANIRU radical, a piperidinyl radical, a pyrazolyl radical, a tetrazolyl group, etc. are mentioned, for example.

[0038] These radicals The same radical as what was expressed as a substituent of the radical expressed with R1 and R2 and an alkyl group can permute.

[0039] A vinyl group, an allyl group, etc. are mentioned as an alkenyl radical expressed with R1 and R2. The alkyl group expressed with R1 and R2 and the substituent expressed as a substituent of an alkyl group, and the same radical can permute these radicals.

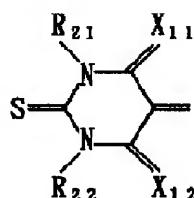
[0040] As a radical which has the acid nucleus shown by E1 in a general formula [1], the radical which has the ossification center indicated by the 15th 14-page line from the 20th 11-page line of JP,61-281235,A, and the radical expressed with the following types 1-4 can be mentioned, for

example.

[0041]

[Formula 6]

式 1

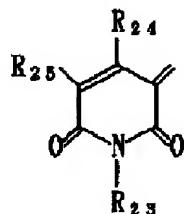


[0042] Among a formula, although R21 and R22 are synonymous with R1 and R2 of said general formula [1], R21 is not the same as that of R22. Moreover, X11 and X12 are synonymous with X1 and X2 in a general formula [1].

[0043]

[Formula 7]

式 2

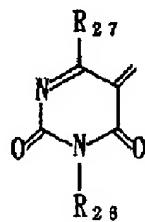


[0044] Among a formula, R23 is synonymous with R1 and R2 in said general formula [1], and R24 and R25 are synonymous with R8-R10 in said general formula [3].

[0045]

[Formula 8]

式 3

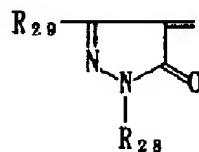


[0046] Among a formula, R26 is synonymous with R1 and R2 in said general formula [1], and R27 is synonymous with R8-R10 in said general formula [3].

[0047]

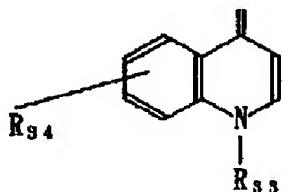
[Formula 9]

式 4



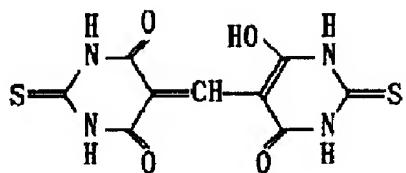
[0048] R28 is synonymous with R1 and R2 in said general formula [1] among a formula. R29 An alkyl group, an aryl group, an alkenyl radical, a heterocycle radical, a cyano group, - COR30, -

- ❖ CON (R30) (R31), -N (R30) (R31), - Express OR30, -SOR30, -SO two R30, -SO2N (R30) (R31), -NR30COR31, -N(R30) SO two R31, -N(R30) CON (R31) (R32), -SR30, and -COOR30.
 [0049] R30-R31 are synonymous with R11-R13 in said general formula [3].
 [0050] The same radical as what was shown by explanation of the point of R1 and R2 as an alkyl group, an alkenyl radical, an above-mentioned aryl group, and an above-mentioned heterocycle radical is mentioned.
 [0051] In the above explanation, although the radical which has the nucleus of the acidity expressed with E1 was expressed with keto form, it thinks chemically and is clear that an enol form can be taken by the tautomerism.
 [0052] What is expressed with the heterocycle and the following formula 5 which were indicated by 23-26 pages of JP,61-282832,A as heterocycle of 5 members formed of Q1 in a general formula [2] or 6 members is mentioned.
 [0053]
 [Formula 10]
 式 5

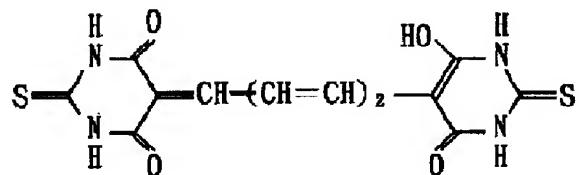


- [0054] Among a formula, R33 is synonymous with R1 and R2 in said general formula [1], and R34 is synonymous with R8-R10 in said general formula [3].
 [0055] the aryl group expressed with W1 in a general formula [5] — carrying out — for example, a phenyl group can be mentioned, a pyridyl radical, a thiazolyl radical, and an oxazolyl radical can be mentioned as a heterocycle radical, and these radicals may have a substituent.
 [0056] Although the typical example of a compound expressed with a general formula [1], [2], [3], [4], and [5] is shown hereafter, this invention is not limited to these.
 [0057]
 [Formula 11]

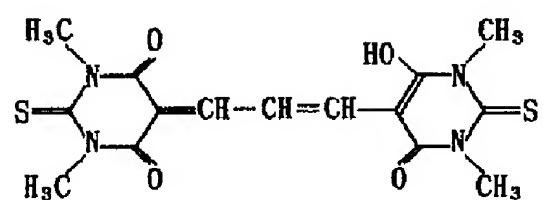
* 1 - 1



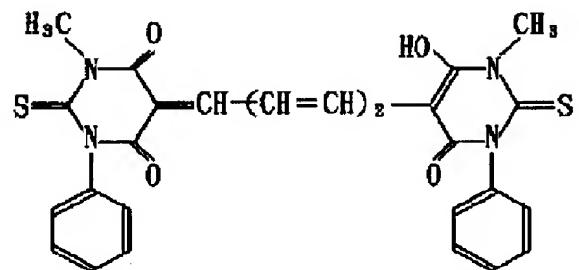
1 - 2



1 - 3

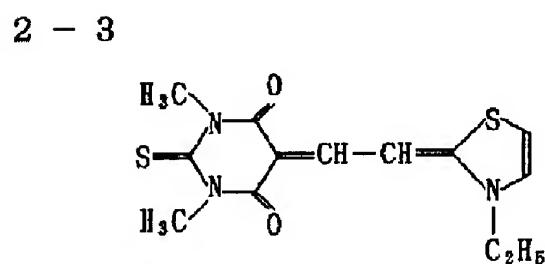
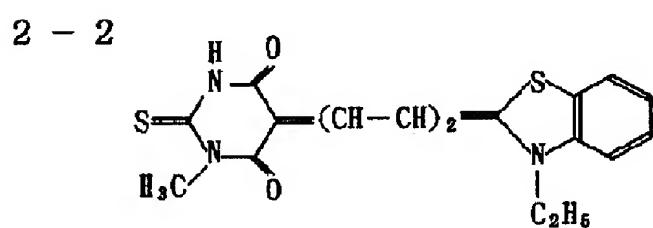
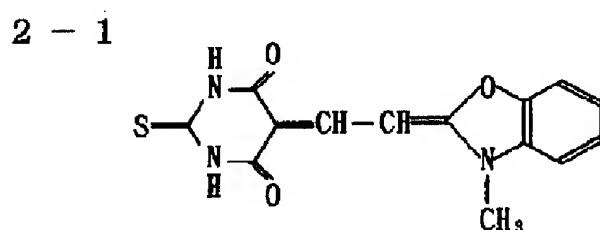
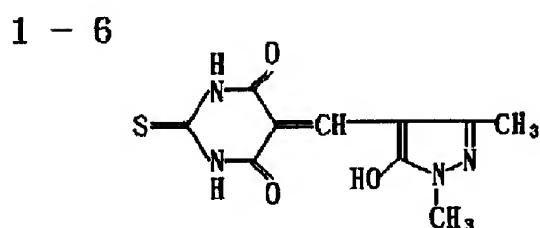
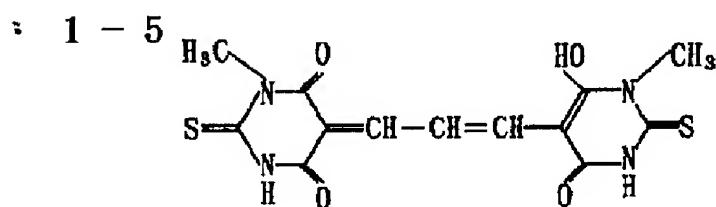


1 - 4



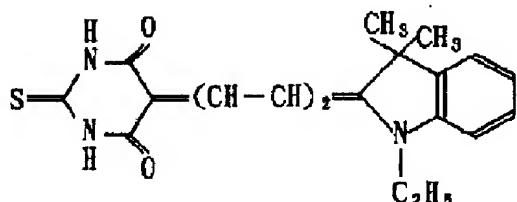
[0058]

[Formula 12]

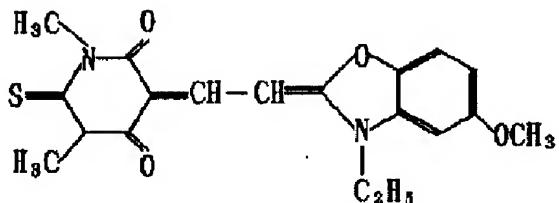


[0059]
[Formula 13]

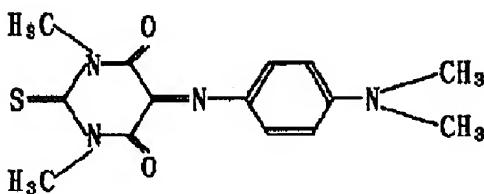
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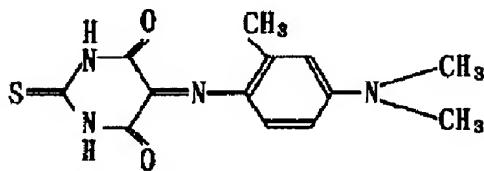
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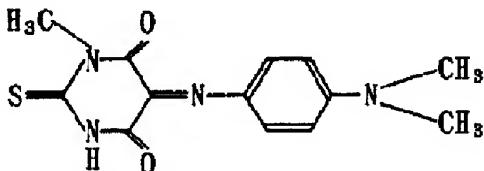
3 - 1



3 - 2



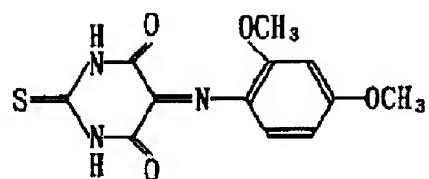
3 - 3



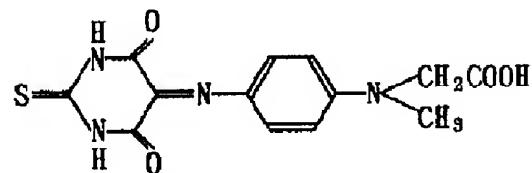
[0060]

[Formula 14]

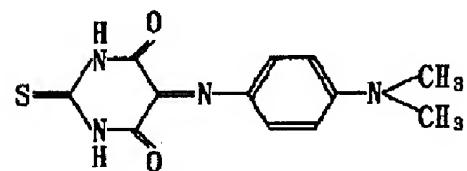
3 - 4



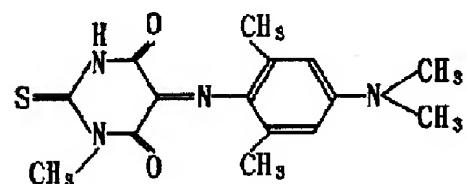
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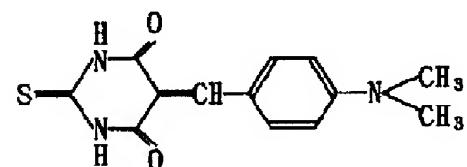
3 - 6



3 - 7



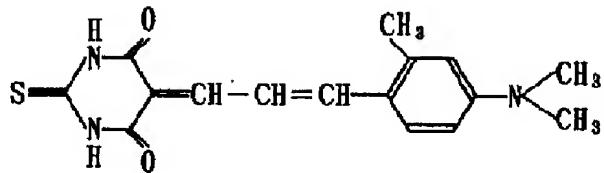
4 - 1



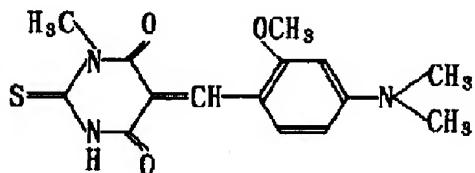
[0061]

[Formula 15]

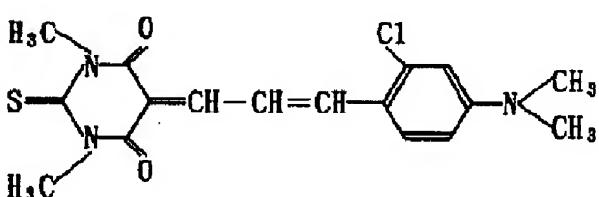
4 - 2



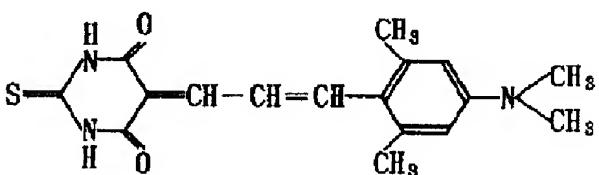
4 - 3



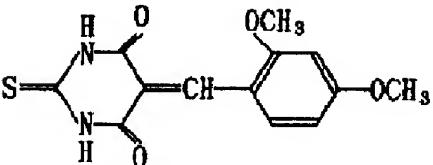
4 - 4



4 - 5



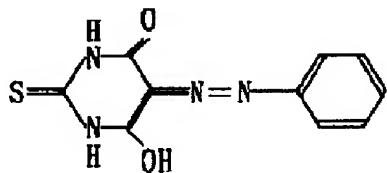
4 - 6



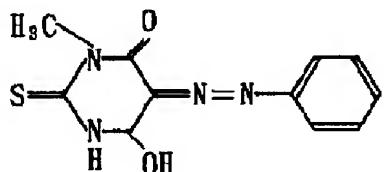
[0062]

[Formula 16]

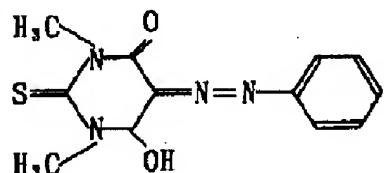
5 - 1



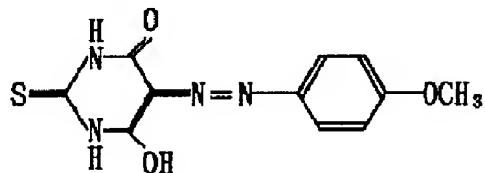
5 - 2



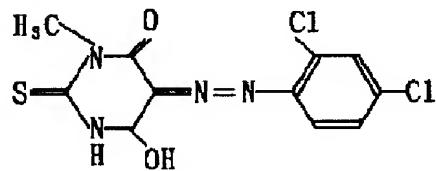
5 - 3



5 - 4



5 - 5



[0063] In addition, as a color preferably used for this invention in addition to the above-mentioned color, the color of a publication can be used [14th page – page / 20th / of the Japanese-Patent-Application-No. No. 189488 / three to / specification by the same people as the applicant of this invention] preferably.

[0064] As a color which can furthermore be used by this invention, the color expressed with following general formula [1']– [5'] other than the above can be mentioned.

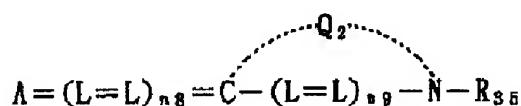
[0065]

[Formula 17]

一般式 [1']



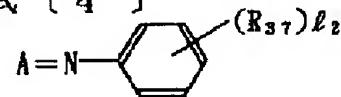
一般式 [2']



一般式 [3']



一般式 [4']



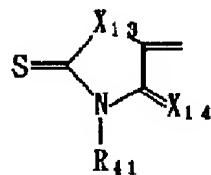
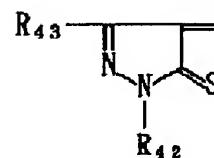
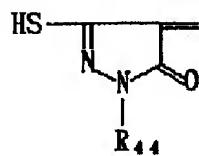
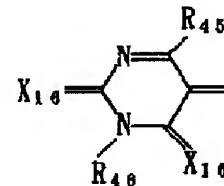
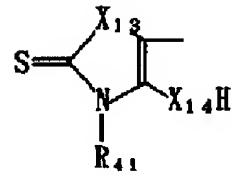
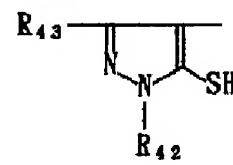
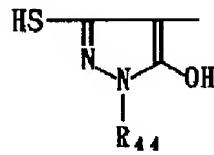
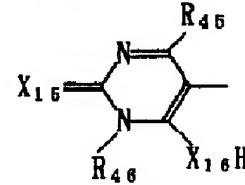
一般式 [5']



[0066] In the above-mentioned general formula [1'] – a general formula [5'] R35 An alkyl group, An alkenyl radical is expressed. R36 and R37 An alkyl group, an alkenyl radical, An aryl group, a heterocycle radical, a halogen atom, a cyano group, a sulfonic group, -COR38, -CON (R38) (R39), -N (R38) (R39), -OR38, -SOR39, -SO two R38, -SO2N (R38) (R39), and -N(R38) COR39 -- or -- Express N(R38) SO two R39, -N(R38) CON (R39) (R40), -SR38, and -COOR38, and R38-R40 express a hydrogen atom, an alkyl group, an alkenyl radical, an aryl group, and a heterocycle radical.

[0067] A expresses the radical expressed with following general formula [A1]- [A4], and A' expresses the radical expressed with following general formula [A'1]- [A'4].

[0068]

一般式 [A₁]一般式 [A₂]一般式 [A₃]一般式 [A₄]一般式 [A'₁]一般式 [A'₂]一般式 [A'₃]一般式 [A'₄]

[Formula 18]

[0069] General formula [In A1]–[A4] and general formula [A'1]–[A'4] R41, R42, R44, and R46 Hydrogen atom, An alkyl group, an alkenyl radical, an aryl group, and a heterocycle radical are expressed. R43 An alkyl group, An alkenyl radical, an aryl group, and heterocycle radical, a cyano group, a sulfonic group, –COR47, –CON (R47) (R48), –N (R47) (R48), –OR47, –SOR47, –SO two R47, –SO2N (R47) (R48), – Expressing N(R47) COR48, –N(R47) SO two R48, –N(R47) CON (R48) (R49), –SR47, and –COOR47, R47–R49 are a hydrogen atom, An alkyl group, an alkenyl radical, an aryl group, and a heterocycle radical are expressed. R46 is synonymous with R36 and R37.

[0070] L expresses a methine group and E expresses the radical which has an acid nucleus. Q2 expresses a nonmetal atom group required to form heterocycle. W2 expresses an aryl group and a heterocycle radical. X13 expresses an oxygen atom, a sulfur atom, a selenium atom, and =N–R50. R50 is synonymous with R41.

[0071] X14, X15, and X16 express an oxygen atom and a sulfur atom. n7 and n8 express n9, 0–3, and n10 express the integer of 0–2, and l1 and l2 express 0–3.

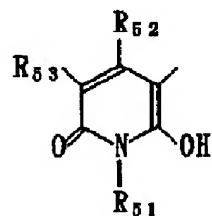
[0072] As an alkyl group expressed with R35–R50 in above-mentioned general formula [1']–[5'], a methyl group, an ethyl group, a propyl group, an isopropyl group, n-butyl, tert-butyl, a cyclopentylic group, a cyclohexyl radical, etc. are mentioned. To these alkyl groups, a hydroxy group, a cyano group, a sulfonic group, a carboxyl group, halogen atoms (for example, a fluorine atom, a chlorine atom, a bromine atom, etc.) and an alkoxy group (for example, a methoxy group --) aryloxy groups (for example, a phenoxy group and 4-sulfo phenoxy group --), such as an ethoxy radical a 2 and 4-disulfo phenoxy group etc. and an aryl group (for example, a phenyl group --) 4s ****s may be carried out to alkoxy carbonyl groups (for example, a

- methoxycarbonyl group, an ethoxycarbonyl radical, etc.), such as 4-sulfophenyl radical, 2, and 5 disulfo phenyl group, and aryloxy carbonyl groups (for example, phenoxy carbonyl group etc.).
 [0073] As an aryl group expressed with R36-R50 and W, a phenyl group and a naphthyl group are mentioned, for example. The alkyl group expressed with R1-R16 and the substituent expressed as a substituent of an alkyl group, and the same radical can permute these radicals.
 [0074] As a heterocycle radical expressed with R36-R50 and W, a pyridine radical, a thiazolyl radical, an oxazolyl radical, an imidazolyl radical, a furil radical, a pyrrolyl radical, a pyrazinyl radical, a pyrimidyl radical, a pilus DAJINIRU radical, the Puri Nils radical, a selenazolyl radical, a sulfo RANIRU radical, a piperidinyl radical, a pyrazolyl radical, a tetrazolyl group, etc. are mentioned, for example. The substituent expressed as a substituent of the alkyl group expressed with R35-R50 and an alkyl group and the same radical can permute these radicals.
 [0075] As an alkenyl radical expressed with R35-R50, a vinyl group, an allyl group, etc. are mentioned, for example, and the substituent expressed as a substituent of the alkyl group expressed with R35-R50 and an alkyl group and the same radical can permute these radicals.
 [0076] As a radical which has the nucleus of the acidity expressed with E in a general formula [1'], the radical expressed with the radical which has the nucleus shown in radical [which has the frame indicated by the 15th page / 14th / line from the 20th page / 11th / line of JP,61-28123,A], and general formula [A'1]-[A'4] and the following general formula [B-I], [B-II], and [B-III] can be mentioned, for example.

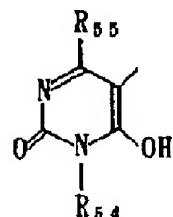
[0077]

[Formula 19]

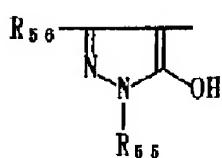
一般式 (B - I)



一般式 (B - II)



一般式 (B - III)

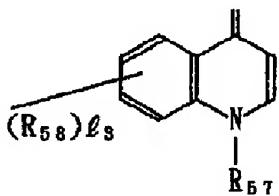


[0078] R51 is synonymous with R41 among a formula, and R52 and R53 express a hydrogen atom and the radical previously shown as R36. R54 is synonymous with R41 and R55 expresses the radical shown as R36 of a hydrogen atom and the point. R55 is synonymous with R42 and R56 is synonymous with R43.

[0079] The heterocycle expressed with the heterocycle and the following general formula [B-IV] which were indicated by 23-26 pages of JP,61-282832,A, for example as heterocycle formed of Q2 in a general formula [2'] can be mentioned.

[0080]

一般式 [B - IV]



[Formula 20]

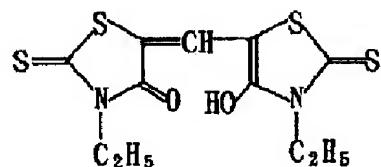
[0081] R_{67} is synonymous with R_{44} among a formula, and R_{58} is synonymous with R_{36} . l_3 is the integer of 0-3.

[0082] Although the typical example of a compound expressed with a general formula [1'] – a general formula [5'] below is shown, this inventions are not these things limited to seeing.

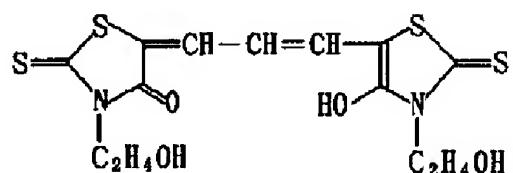
[0083]

[Formula 21]

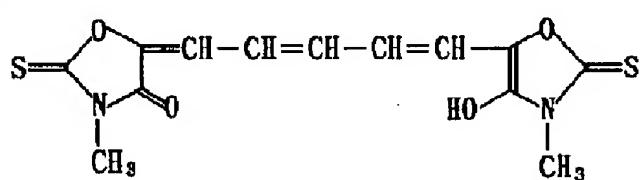
1' - 1



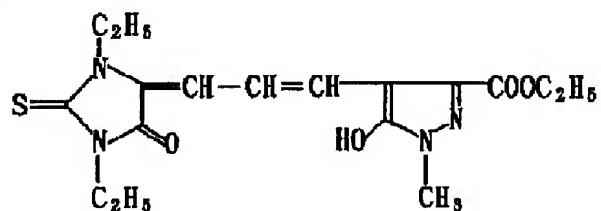
1' - 2



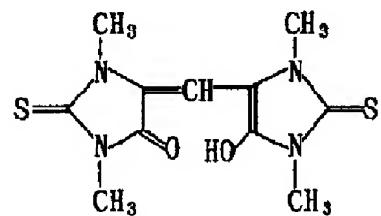
1' - 3



1' - 4



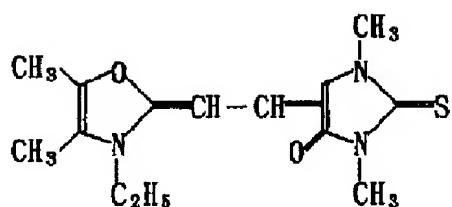
1' - 5



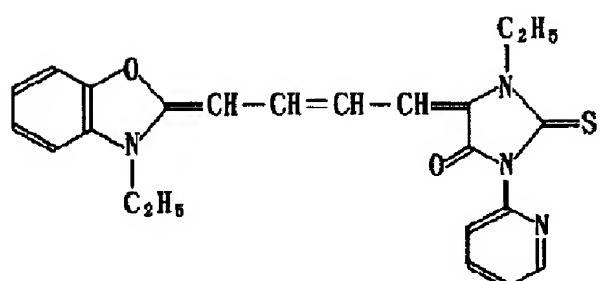
[0084]

[Formula 22]

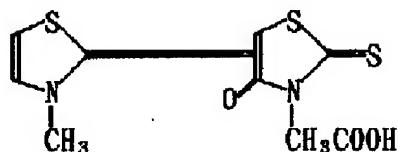
2' - 1



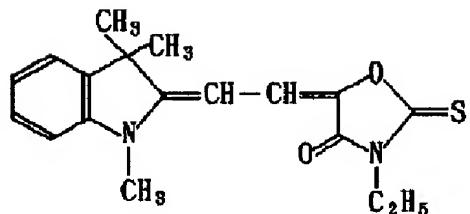
2' - 2



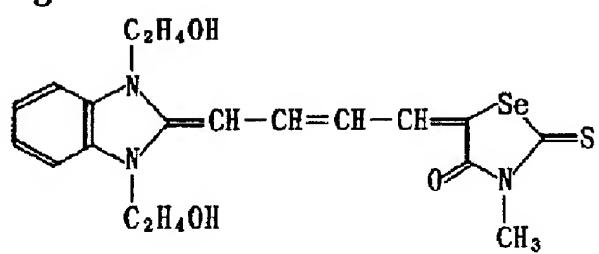
2' - 3



2' - 4



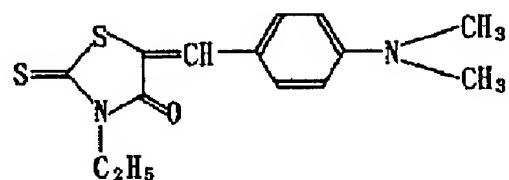
2' - 5



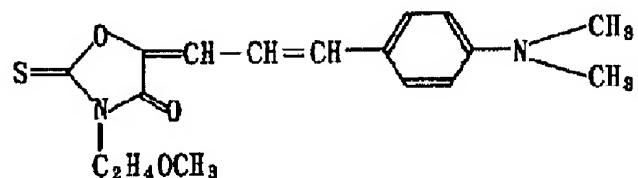
[0085]

[Formula 23]

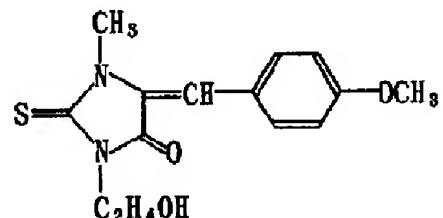
3' - 1



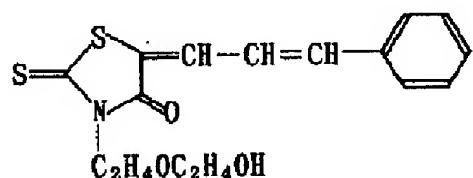
3' - 2



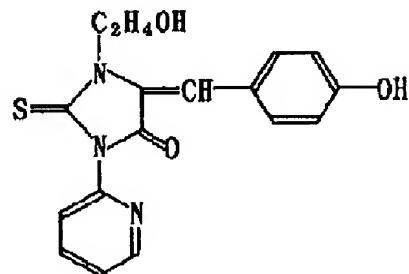
3' - 3



3' - 4



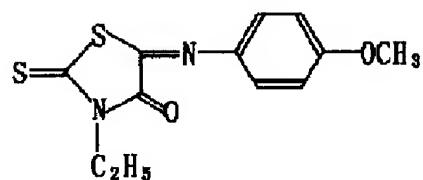
3' - 5



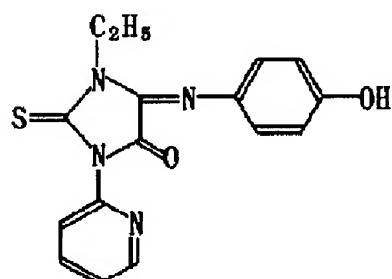
[0086]

[Formula 24]

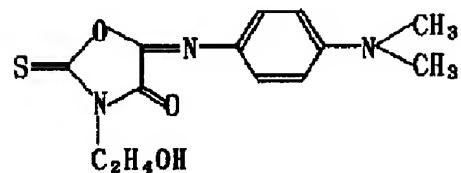
4'-1



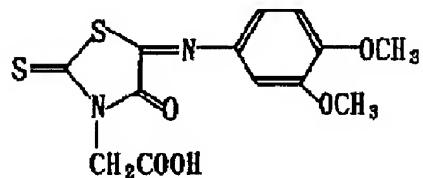
4'-2



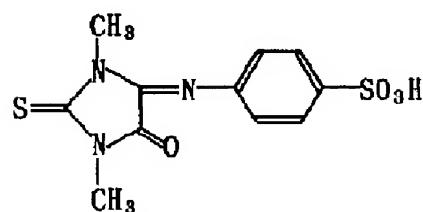
4'-3



4'-4



4'-5



[0087]
 [Formula 25]



ID=000026

[0088] In addition, as a color preferably used for this invention in addition to the above-mentioned color, it is the Japanese Patent Application No. by the same people as the applicant of this invention. The color of a publication can be used [26th page - page / 34th / of 3 No. - 189488 specification] preferably.

[0089] Furthermore, as a color which can be preferably used for this invention, the color expressed with the following general formula [6] is mentioned.

[0090]

A general formula [6] Dye expresses the atomic group which has methine dye structure among $n_1[-(J)n_2-Sal]n_3$ type. (Dye) J expresses the divalent connection radical which makes an ossification center the atom or atomic group chosen from a carbon atom, a nitrogen atom, an oxygen atom, and a sulfur atom, Sal expresses the radical which forms complex ion and a poorly soluble salt, in n_1 , 1 or 2, and n_2 express 0 or 1, and n_3 express 1-4.

[0091] The radical shown by Dye in the above-mentioned general formula [6] is a radical which

has the color structure where express the atomic group which has methine dye structure, for example, conjugated double bond of the methine chains, such as cyanine, merocyanine, MEROSUCHIRIRU, styryl, oxo-Norian, and thoria reel methane, is carried out. As an example of these colors, for example, JP,63-202665,A, Cyanine dye given in Soviet country JP,653,257,B, JP,52-29727,A, 52-60825, 52-135335, 56-27146, 56-29226, 59-10944, 59-15934, 59-111847, 63-34539, a U.S. Pat. No. 2,944,896 number, A merocyanine color given [this] in No. 3,148,187, JP,52-211041,A, 59-211042, 60-135936, 60-135937, 61-204630, 61-205934, 62-56958, A MEROSUCHIRIRU color given in 62-70830, 62-92949, 62-185758, etc., JP,50-145125,A, 55-33103, 55-120660, 55-161233, 62-185755, 63-139949, 63-231445, 63-264745, a U.S. Pat. No. 4,187,275 number, The thoria reel methane color of a publication is mentioned to an oxo-Norian color given in British JP,1,B, No. 521083, Belgium country JP,869,677,B, etc., JP,59-55437,A, 59-228250, a U.S. Pat. No. 4,115,126 number, said 4,359,574 numbers, etc.

[0092] further -- the volume on T.H.James "The Theory of the Photographic process" -- the 4th edition Macmillan Co. ** (1977), F. "Heterocyclic Compound Cyanin Dyes and related Compound" John Wiley & Sons(New York London)1964 written by M Hamer annual publication, D. edwritten by M Sturmer "The Chemistry of Heterocyclic Compounds" A.Weiss berger and E.C.Taylor, 1977 annual publications, " -- The Chemistry of Synthetic Dyes" Academic press (New York London) Vol.11 and 1952 annual publications -- said -- it is chosen from what is indicated by compendiums, such as Vol.IV and 1971 annual publications.

[0093] J in a formula expresses the divalent connection radical which makes a frame the atom or atomic group chosen from a carbon atom, a nitrogen atom, an oxygen atom, and a sulfur atom. a desirable radical -- an alkylene group (for example, methylene, ethylene, and a propylene --) Propine radicals, such as a pentene radical s (for example, phenylene group etc.) Alkenylene group (for example, propine radical etc.), A sulfonyl group, a sulfinyl group, a ether group, a thioether radical, a carbonyl group, - N (R59) radical (R59 -- a hydrogen atom, a permutation, or an unsubstituted alkyl group --), a permutation or an unsubstituted aryl group, a -N= radical, and a heterocycle divalent radical (for example, triazine -2 and 4-diyl radical --) It is a with a carbon number of 20 or less constituted combining a pyrimidine -2, 4-diyl radical, a thiazole -2, 4-diyl radical, the benzoxazole -2, 5-diyl radical, etc. one or more than it divalent connection radical, and you may have the substituent.

[0094] the general thing as a substituent mentions -- having -- a halogen atom (for example, a fluorine atom --) alkyl groups (for example, methyl, ethyl, and isopropyl --), such as a chlorine atom and a bromine atom aralkyl radical (for example, benzyl, phenethyl radical, etc.) alkoxy groups (for example, methoxy --), such as butyl Alkoxy carbonyl groups, such as ETOKISHI (for example, ethoxycarbonyl radical etc.), an alkylthio group, a hydroxy group, a carboxy group, a sulfonic group, and a sulfonyl group (for example, a methane sulfonyl group --) carbamoyl groups (for example, N-methylcarbamoyl radical --), such as a p-toluenesulfonyl group acyl groups (for example, an acetyl group --), such as a morpholino carbonyl sulfamoyl group Acyl amide groups, such as benzoyl (for example, acetamide radical etc.), The radical of arbitration, such as sulfonamide radicals (for example, methane a pickpocket a phone amide group, a butane sulfonamide radical, etc.), a cyano group, amino groups (for example, an ethylamino radical, a dimethylamino radical, etc.), and an ureido radical, is chosen.

[0095] In n1 in a formula, n2 express 0 or 1 and n3 express 1, 2, 3, or 4 for 1 or 2.

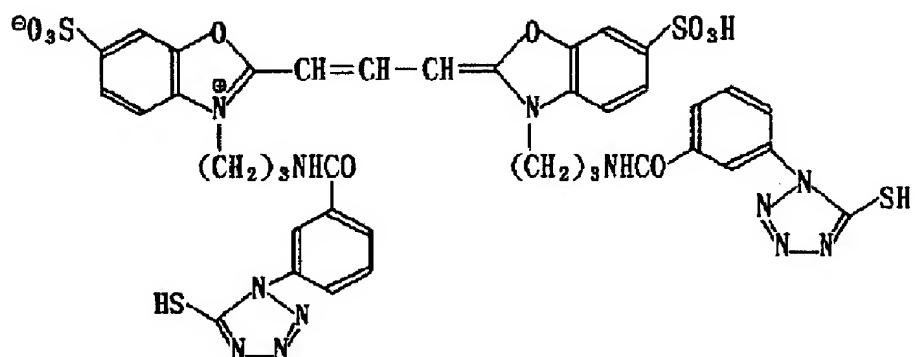
[0096] The heterocycle residue of 5 - 7 member of the saturation or partial saturation included in endocyclic is mentioned [atom / a front base material, for example, a sulphydryl group, an acetylenic group, a thiocarbonyl group, a thioamide radical, a thio urethane group, thio ureido radicals (for example, 3-ethyl thio ureido radical, 3-phenylthio ureido radical, etc.), or / at least one / nitrogen] in the radical in which Sal forms complex ion and a poorly soluble salt. The radical shown as a desirable radical by given in JP,2-97937,A general formula (VII), radical [which is shown by (IX)], or given in JP,2-225476,A general formula (II)- (VI) is mentioned.

[0097] Although the concrete compound of the color expressed with the general formula [6] of this invention is shown hereafter, this invention is not limited to these.

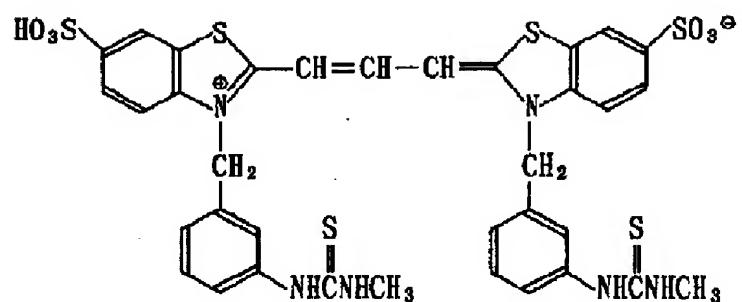
[0098]

[Formula 26]

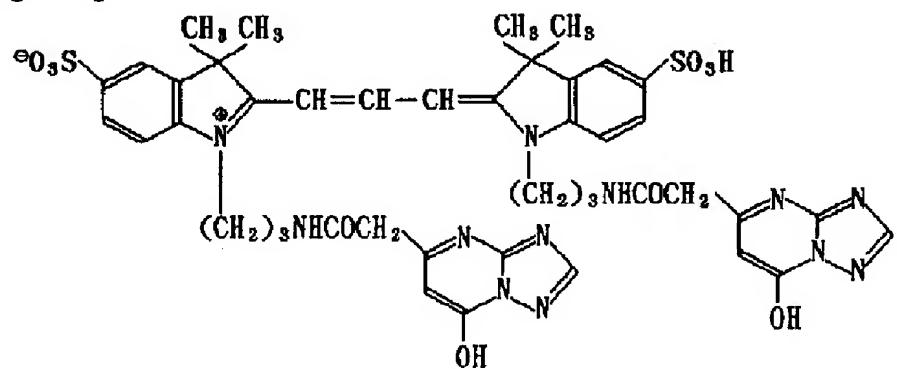
6 - 1



6 - 2



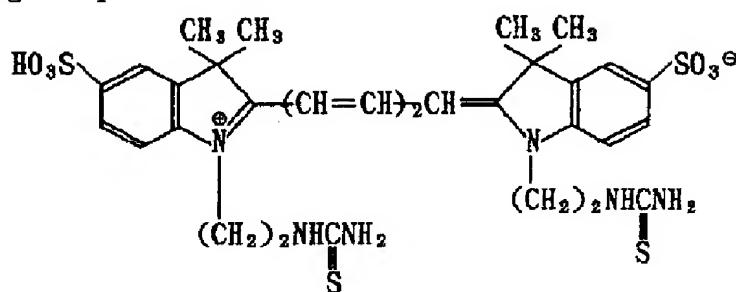
6 - 3



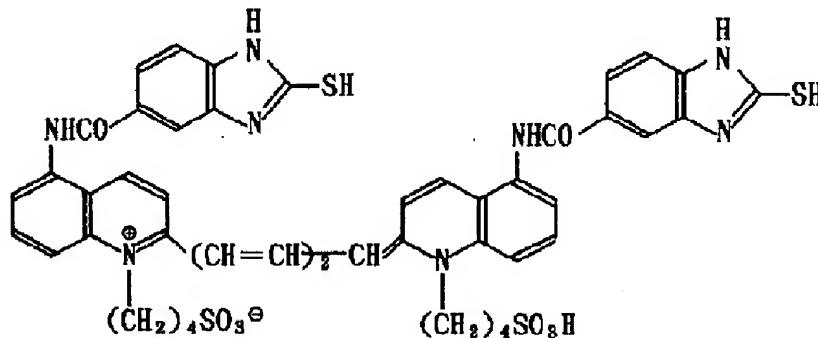
[0099]

[Formula 27]

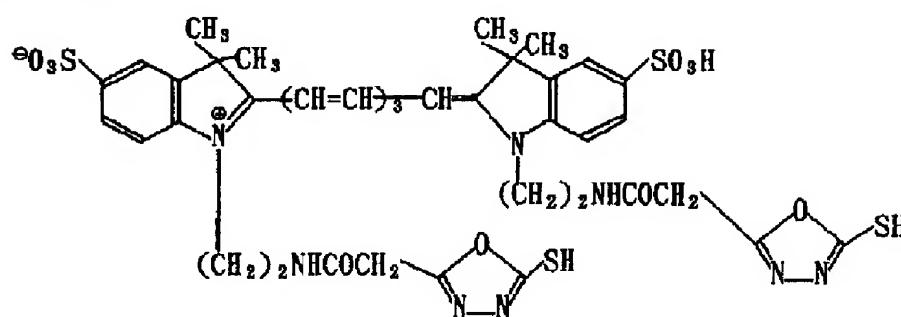
6 - 4



6 - 5



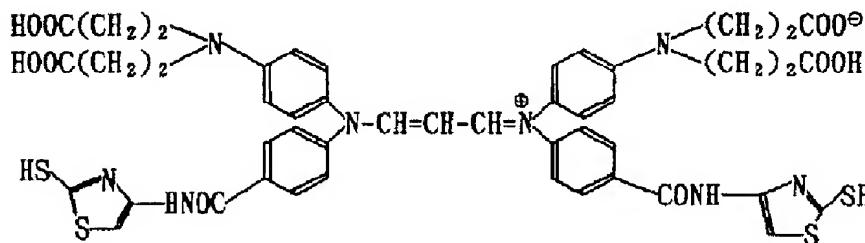
6 - 6



[0100]

[Formula 28]

6 - 7



[0101] In addition, as a color preferably used for this invention in addition to the above-mentioned color, the color of a publication can be used [38th page – page / 39th / of the Japanese-Patent-Application-No. No. 189488 / three to / specification by the same people as the applicant of this invention] preferably.

[0102] Any of the approach of colorizing from the intermediate-product raw material which permuted the poorly soluble silver salt formation radical beforehand shown by Sal, and the approach of combining a part for the methine dye structured division shown by Dye and a Sal

part are sufficient as the methine dye concerning this invention, and selection composition can be carried out at arbitration.

[0103] Installation of a Sal radical can use various well-known ligation reactions. For example, the substitution reaction of active hydrogen substituents, such as an addition reaction to partial saturation radicals, such as a vinyl group and a carbonyl group, an amino group, and a hydroxy group, and an acid derivative and a halogen derivative can perform. It faces performing these reactions. Composition of the organic chemistry edited "the new experimental science lecture 14" by the Chemical Society of Japan, and reaction I-V volume (Maruzen) 1962 annual publication, "Organic Reactions" Vol. 1 and 3, and 12 John Wiley&Sons (New York London), "The Chemistry of functional Groups" John Wiley&Sons (New York London), It can refer to many compendiums, such as "Advanced Organic Chemistry" L.F.Fieser and M.Fieser and 1962 (Maruzen) annual publications.

[0104] The above-mentioned color of this invention is made to react with a fusibility silver salt water solution, is made into poorly soluble silver salt, and carries out distributed addition of this into silver halide sensitive material.

[0105] Next, when making the above-mentioned color silver salt contain in the hydrophilic colloid layer of the Bth page of the sensitive material in this invention, color silver salt is attached, 0.01 – 2.0 g/m² of an amount is desirable, and especially 0.05 – 1.0 g/m² is desirable [an amount]. 0.3 – 1.5 g/m² is desirable, and the amount with gelatin of a hydrophilic colloid layer has desirable 0.5 – 1.0 g/m².

[0106] In addition, you may be hydrophilic colloid which carried out concomitant use content of the well-known color besides the above-mentioned color silver salt at the silver halide photosensitive material of this invention.

[0107] The emulsion used for the silver halide photosensitive material of this invention can be manufactured by the well-known approach. For example, it can prepare by 1, an emulsion manufacturing method (Emulsion Preparation and types), and the approach of (** RD) No.18716 (November, 1979) and a 648-page publication (research (disclosure RD) No.17643 (December, 1978) and 22-23 pages).

[0108] The emulsion of the silver halide photosensitive material concerning this invention for example, T.H.James work "The theory of the photographic process" -- the 4th edition The approach of a 38-104 page [of Macmillan Co. **] (1977) publication, G. -- F.Dauffin work -- "photographic-emulsion chemistry "Photographic Emulsion Chemistry"" -- Focal press Company ** (1966), and physics of a photograph and "chemistry" "Chimie et physique photographique" PaulMontel written by P.Glafkides Company ** (1967), V. L.Zelikman Manufacture of a photographic emulsion, and other work "spreading" "Making and Coating photographic Emulsion" Focal press It is prepared by company ** (1964) etc. by the approach of a publication.

[0109] That is, it can manufacture using particle preparation conditions and these combination methods, such as mixed conditions, such as order alligation, a back-mixing method, a double jet process, and a controlled double jet method, the conversion method, and a core/Shell process, on solution conditions, such as a neutral process, acid process, and the ammonia method. As a desirable example, the mono dispersion emulsion which carried out localization of the silver iodide to the interior of a particle is mentioned.

[0110] Mono dispersion is a dispersed system by which 95% or more of particle goes into less than **40% of size of number average particle size here. Number average particle size is a number average diameter of the projected area diameter of a particle here. Although the internal structure of the silver halide particle used for this invention is arbitrary, the thing of the core shell structure where silver halide presentations differ is desirable.

[0111] Shell is formed by covering with silver halides, such as iodine silver bromide, salt iodine silver bromide, silver chlorobromide, a silver bromide, and a silver chloride. Especially preferably, from an outside surface, 0.01 micrometers or more, a shell part with a thickness of 0.01–0.5 micrometers is iodine silver bromide containing less than [10 mol %], and silver iodide silver iodide It is formed by the iodine silver bromide not more than 5 mol %.

[0112] When using seed crystal, at least 20% or more of silver bromide may be formed only in

seed crystal, and you may cover with a shell layer after this. or [or / setting the amount of silver iodide of seed crystal to 0] — or it may consider as within the limits not more than 10 mol %, at least 20% or more of silver iodide may be made to form in the interior of a particle at the process into which seed crystal is grown up, and you may cover with a shell layer after this. [0113] Moreover, the silver halide particle which has the localization part which 20% or more of high-concentration silver iodide localized can use it preferably. As for 20% or more of such a high concentration silver iodide localization part, it is desirable that a localization part exists in the part which separated 0.01 micrometers or more from the outside surface of a particle.

[0114] Moreover, a localization part may exist in the shape of a layer inside a particle, core shell structure may be taken, and the whole core may serve as a localization part. In this case, it is desirable that a part thru/or all of the particle core section excluding a shell part with a thickness of 0.01 micrometers or more from an outside surface is the localization part of the silver iodide concentration beyond 20 mol %. As for the silver iodide of a localization part, it is more desirable that the concentration is 30–40–mol %.

[0115] A plate-like silver halide particle is preferably mentioned to the emulsion of the silver halide photosensitive material of this invention.

[0116] 0.2–2.5 micrometers is desirable especially desirable, and the mean particle diameter of a plate-like silver halide particle is 0.5–2.0 micrometers. The average (it is called an average aspect ratio) of a particle diameter/thickness (it is called an aspect ratio) is two or more, and a plate-like silver halide emulsion is three or more preferably, and are 5–10 especially preferably.

[0117] Moreover, the average thickness of a plate-like silver halide emulsion has desirable 0.4 micrometers or less, and 0.3 micrometers or less are 0.05–0.25 micrometers especially preferably more preferably.

[0118] That whose plate-like silver halide emulsion is mono dispersion nature is used preferably, the silver halide particle contained in **20% of size range focusing on mean particle diameter is especially desirable, and 50% of the weight or more of a thing is used.

[0119] A plate-like silver halide emulsion has desirable silver iodochlorobromide from the point of high sensitivity, although the silver halide presentation is arbitrary at a silver chloride, a silver bromide, salt silver iodide, silver chlorobromide, iodine silver bromide, salt iodine silver bromide, etc., the average silver iodide content in this case is 0–4.0–mol %, and it is especially average silver chloride content at 0.2–3.0–mol % preferably. It is 0–5–mol %.

[0120] Moreover, although a plate-like silver halide emulsion may have a uniform silver halide presentation within a particle and silver iodide may carry out localization, what carried out localization is preferably used for a core.

[0121] The manufacture approach of a plate-like silver halide emulsion can also refer to JP,58-113926,A, 58-113927, 58-113934, 62-1855, the European Patent No. 219,849, said 219,850 numbers, etc.

[0122] Moreover, it can refer to JP,61-6643,A as the manufacture approach of the plate-like silver halide emulsion of mono dispersion nature.

[0123] As the manufacture approach of a plate-like iodine-silver-bromide emulsion with a high aspect ratio, a silver-nitrate water solution or a silver-nitrate water solution, and a halogenide water solution are added at coincidence in the gelatin water solution with which pBr was kept or less at two, seed crystal is generated, and it can obtain by next making it grow up with a double jet process.

[0124] The magnitude of a plate-like silver halide particle is controllable with the addition rate of the temperature at the time of particle formation, silver salt, and a halogenide water solution.

[0125] The average silver iodide content of a plate-like silver halide emulsion is controllable by changing the presentation of the halogenide water solution to add, i.e., the ratio of a bromide and an iodide.

[0126] Moreover, silver halide solvents, such as ammonia, a thioether, and thiourea, can be used if needed at the time of manufacture of a plate-like silver halide particle.

[0127] In order that an emulsion may remove fusibility salts, the rinsing approaches, such as the noodle rinsing method and a flocculation sedimentation method, may be made. As a desirable rinsing method, the approach using the approach using the aromatic hydrocarbon system

aldehyde resin which contains a sulfonic group given in JP,35-16086,B, for example or condensation macromolecule agent instantiation G3 given in JP,63-158644,A, G8, etc. is especially mentioned as a desirable desalting method.

[0128] In the process before and behind physical aging or chemical ripening, various kinds of additives for photographs can be used for the emulsion concerning this invention, as a well-known additive -- research disclosure No.17643 [for example,] (December, 1978) -- said -- No.18716 (November, 1979) -- and -- said -- the compound indicated by No.308119 (December, 1989) is mentioned. The compound class and written part which are shown in these three research disclosure were carried below.

[0129]

An additive RD-17643 RD-18716 RD-308119 A page A classification A page A classification A page Classification Chemical sensitizer 23 III 648 Upper right 996 III Sensitizing dye 23 IV 648-649 996-8 IV Desensitizing dye 23 IV 998 B Accelerator 29 XXI 648 Upper right A fogging inhibitor and stabilizer 24 IV 649 The upper right 1006 - 7 VI brightening agent 24 V 998 V hardening agent 26 X 651 Left 1004-5 X Surfactant 26-7 XI 650 Right 1005-6 XI Antistatic agent 27XII 650 Right 1006-7 XIII Plasticizer 27 XII 650 Right 1006 XII Slide agent 27 XII Mat agent 28 XVI 650 Right 1008-9 XVI Binder 26XXII 1003-4 IX Base material 28 XVII 1009 What is indicated by the above-mentioned 28 pages of RD-17643 and 1009 pages of RD-308119, for example as a base material which can be used for the sensitive material concerning XVII this invention is mentioned.

[0130] As a suitable base material, it is plastic film etc., and in order to receive adhesion of a spreading layer, the front face of these base materials may prepare undercoat, or may perform corona discharge, UV irradiation, etc.

[0131]

[Example] Hereafter, this invention is not limited by the following examples although an example explains this invention.

[0132] It is silver iodide with a mean particle diameter of 0.2 micrometers with a double jet process, controlling to 160 degrees C of preparation of an example 11 kind emulsion, pAg=8, and pH=2.0. The mono dispersion legislation crystallite child of the iodine silver bromide containing two-mol % was prepared. It is the Kao atlas company make at 40 degrees C about the obtained reaction mixture, After desalting using a DEMORU water solution and a magnesium sulfate mixture solution A gelatin water solution is added and it re-distributes, The seed emulsion was obtained., 2) The particle was grown up as follows using the growth 1 above-mentioned seed emulsion from a seed emulsion. Into the gelatin water solution first kept at 40 degrees C, the above-mentioned seed emulsion was distributed and aqueous ammonia and an acetic acid adjusted pH further 9.7. The ammonia nature silver-nitrate ion water solution and the water solution of a potassium bromide and a potassium iodide were added with the double jet process in this liquid. During addition, pAg=7.3 and pH were controlled to 9.7 and the silver iodide content % of layer of 35 mols was formed. next, an ammonia nature silver-nitrate water solution and a potassium-bromide water solution -- double JIEETO -- it added by law. 95% of target particle size kept at pAg=9.0, and it changed pH even to 9.0-8.0 continuously. After that It was made to grow up to target particle size, adjusting pAg to 11.0 and keeping pH at 8.0. Then, the gelatin solution was added and it re-distributed, after lowering pH to 6.0 with the acetic acid, adding 400mg per one mol of silver halides of anhydrides of 5 and 5'-dichloro-9-ethyl -3 and 3'-G (3-sulfopropyl) OKISA carbocyanine sodium salt and desalting using an aforementioned DEMORU water solution and an aforementioned magnesium sulfate mixture solution.

[0133] 14 roundish [wore average silver iodide content % of the top-most vertices of 2.0 mols by this approach] one -- mean particle diameter 0.35 micrometers, 0.40 micrometers, 0.65 micrometers, and coefficient of variation -- respectively -- 0.17 and 0. --- (A), (B), and (C) were prepared for the mono dispersion iodine-silver-bromide emulsion of 16 and 0.16.

[0134] After adding a mol of a potassium-bromide water solution -- a silver-nitrate water solution and hydrogen-peroxide processing gelatin are included -- in the 0.05-N potassium-bromide water solution containing the hydrogen-peroxide processing gelatin violently agitated at 230 degrees C of preparation of the preparation 21 kind emulsion of an emulsion with the double

jet process, applying to it for 30 minutes after after 1.5 minutes and lowering solution temperature to it to 25 degrees C, 80ml [per one mol of silver nitrates] aqueous ammonia (28%) was added, and churning was continued for 5 minutes.

[0135] Then, after doubling pH with 6.0 with the acetic acid and desalting using a DEMORU water solution and a magnesium sulfate mixture solution, the gelatin water solution was added and it re-distributed. The obtained seed emulsion was the ball-shaped particle of the mean particle diameter of 0.20 micrometers, and coefficient of variation 0.28.

[0136] 2) The particle was grown up as follows using the growth 2 above-mentioned seed emulsion from a seed emulsion.

[0137] The water solution and silver-nitrate water solution of a potassium bromide and a potassium iodide were added with the double jet process in the ossein gelatin violently agitated at 75 degrees C, and the water solution containing propyleneoxy-polyethyleneoxy-disuccinate-disodium salt.

[0138] It kept at pH=5.8 and pAg=9.0 in the meantime. The addition termination back pH was doubled with 6.0, and the anhydride of 5 and 5'-dichloro-9-ethyl -3 and 3'-G (3-sulfopropyl) OKISA carbocyanine sodium salt was added per one mol of silver halides. After desalting using a DEMORU water solution at 40 more degrees C, the gelatin water solution was added and it re-distributed.

[0139] The projected-area diameter of 0.76 micrometers and 0.25 aspect ratio coefficient of variation prepared the plate-like iodine-silver-bromide emulsion (D) of 3.6 at average silver iodide content % of 1.5 mols by this approach.

[0140] The preparation profit **** emulsion (A) of a sample, (B), (C), and (D) are alike, respectively. At 55 degrees C, 5 and 5'-dichloro-9-ethyl -3, 3'-G The anhydride of OKISA carbocyanine sodium, and the anhydride of 5 and 5'-G (butoxycarbonyl) -1, the 1'-diethyl -3, and 3'-G (4-sulfo butyl) benzoimidazolo carbocyanine sodium salt (3-sulfopropyl) By the weight ratio of 200:1 975mg and (B) added [per one mol (A) of silver halides], and 390mg and 500 (mg of D) added [600mg and (C)]. After 10 minutes, chloroauric acid, a sodium thiosulfate, and ammonium thiocyanate were added to the suitable amount, and chemical ripening was performed. 200mg hand addition per one mol of silver halides of the potassium iodide is carried out at aging termination 15 quota, and it is 4-hydroxy-6-methyl after that. - 1, 3, 3a, and 3xten - two mol per one mol of silver halides of 7-tetra-ZAINNDEN were added, and it distributed in the water solution containing 70g of gelatin. Among four kinds of emulsions [finishing / aging], while it had been independent, it considered as Emulsion A, it mixed at a rate of 75:25 by the weight ratio, and (B) and (C) used (A) as Emulsion B, and while it had been independent, it used (D) as Emulsion C.

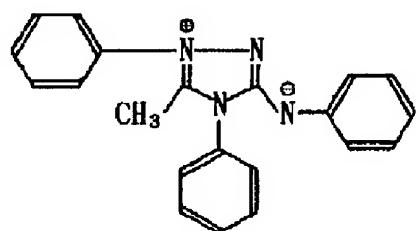
[0141] The following additive was added to each of Emulsion A, Emulsion B, and Emulsion C, and it considered as photosensitive silver halide emulsion coating liquid. The additive is as follows and an addition is a silver halide. 1 The amount per mol shows.

[0142]

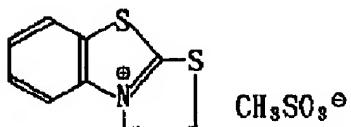
1 and 1-dimethylol-1-bromine-1-nitromethane 70mg t-butyl-catechol 400mg Polyvinyl pyrrolidone (molecular weight 10,000) 1.0mg Styrene maleic anhydride copolymer 2.5g Nitrophenyl-triphenyl phosphonium chloride 50mg 2-ANIRINO -4, 6-dimercapto triazine 60mg 1, 3-dihydroxybenzene-4-sulfonic-acid ammonium 4g 2-mercaptop Benz imidazole-5-sulfonic-acid sodium 1.5mg C4H9OCH2CH(OH) CH2N2 (CH2COOH) 1g 1-phenyl-5-mercaptop tetrazole 15mg

[0143]

[Formula 29]



150mg



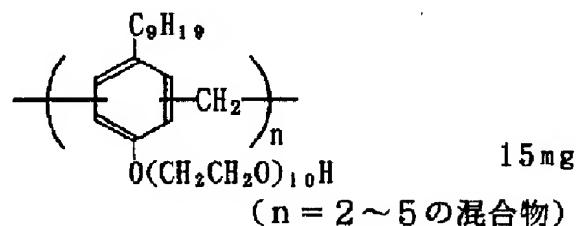
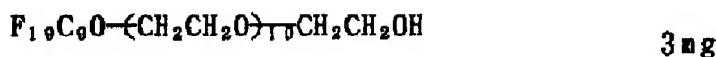
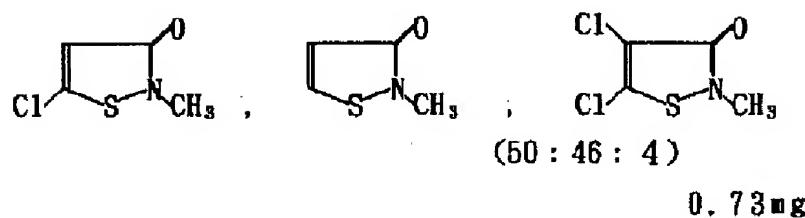
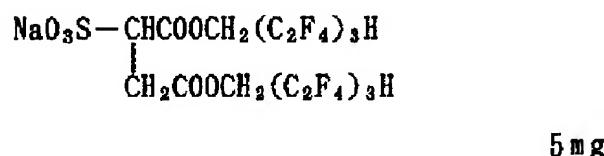
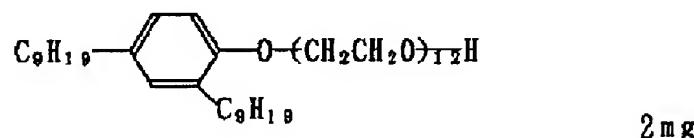
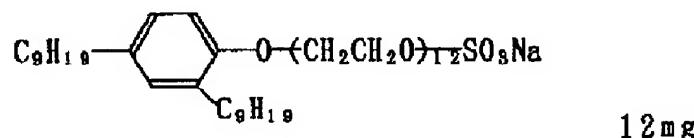
30mg

[0144] Moreover, the additive used for protective layer liquid is as follows, and the amount per 1l. of coating liquid shows an addition.

[0145]

Liming inert gelatin 68g Acid-treatment gelatin 2g Sodium-i-amyl-n-decyl sulfosuccinate 0.3g Polymethylmethacrylate (mat agent with an area mean particle diameter of 3.5 micrometers) 1.1g Silicon dioxide (mat agent with an area mean particle diameter of 1.2 micrometers) 0.5g RUDOKKUSU AM (Du Pont colloidal silica) 30mg 2 and 2-dichloro-6-hydroxy-1,3,5-triazine sodium salt 2% water solution 10ml Glyoxal 40% water solution 1.5ml ($\text{CH}_2=\text{CHSO}_2\text{CH}_2$) 20 300mg [0146]

[Formula 30]



[0147] In addition, as a sample concerning this invention as shown in the following table 1, the emulsion of the Ath page and the Bth page was constituted, and it considered as the sample.

[0148]

[Table 1]

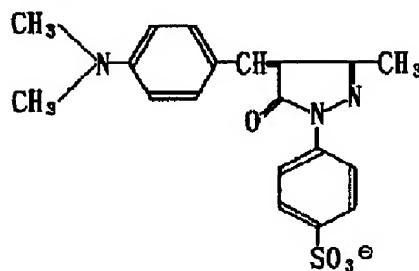
層構成 No.	A面			B面		
	乳剤	銀付量 (g/m ²)	最高濃度	乳剤	銀付量 (g/m ²)	最高濃度
I	B	3.65	3.45	—	—	—
II	B	1.8	1.73	B	1.8	1.73
III	B	1.8	1.73	A	1.5	1.75
IV	B	2.0	1.92	A	1.3	1.52
V	B	2.0	1.92	A	1.5	1.75
VI	C	1.8	2.01	A	1.3	1.77
VII	C	1.8	2.01	A	1.5	2.10
VIII	C	2.0	2.20	A	1.3	1.77

[0149] Moreover, the protective layer coating liquid on the emulsion of the Bth page prepared and applied the protective layer coating liquid which contains the backing color for a comparison (following), and the color silver salt of this invention as shown in Table 2.

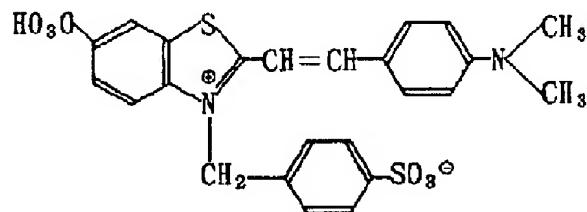
[0150]

[Formula 31]

パッキング染料 (A)



パッキング染料 (B)



[0151] about 1-22 of the evaluation approach photograph engine-performance profit *** sample film of the engine performance Konica imaging camera of P-45 fluorescent-substance use Type - MM (product made from the Konica [stock]) is used. With gray scale 1 / after exposing for 2 seconds, The assignment formula of auto-processor SRX-502, developer XD-SR, and fixer XF-SR (all are the products made from the Konica [stock]) is used. The development temperature of 35 degrees C, 5l./m was supplied at 18 degrees C, the fixing temperature of 33

degrees C and rinsing water were processed in all the down-stream-processing 45-second modes, the sensitometry curve was obtained, and relative sensibility and fogging were searched for.

[0152] Moreover, by removing the sensitization layer by the side of the Bth page of 1-22 of the applied film with a proteolytic enzyme, it asked for the Ath page of concentration, and the concentration of the Bth page was measured by removing the sensitization layer of the Ath page from a sample similarly. It asked for the concentration DB of the Bth page in the light exposure to which the concentration of the Ath page becomes fogging +1.10 from this. The value of sensibility is brightness (it asked as the inverse number of the value measured by Minolta TV Color Analyzer TV -2170 and Probe No.103054 (product made from the Minolta [stock]), and expressed with the relative sensibility when setting sample No.1 to 100.) required to obtain the concentration of fogging +1.10.

[0153] sharp -- the pattern of SMPTE recommendation (Society of Motion Pictureand Television Engineers establishment, Japanese Society of Medical Imaging Technology) was photoed for sharp nature as evaluation of the image quality of sex sample No.1-19, and resolution was evaluated by viewing by the following criteria about the high contrast pattern and the low contrast pattern.

[0154] About the remaining color nature resulting from the evaluation color coloring matter of remaining color nature discriminable to E:5 pixels discriminable to D:4 pixels discriminable to C:3 pixels discriminable to B:2 pixels discriminable to the valuation basis of A:1 pixel, 35 degrees C of unexposed quarter size films were processed for 45 seconds using auto-processor SRX-501, developer XD-SR, and fixer XF-SR, and the processing film was evaluated by viewing on the light source base for photograph observation.

[0155] Valuation basis A: B without the coloring-matter remainder: The coloring-matter remainder is C which does not have trouble in a diagnosis although it is slightly. : D which the coloring-matter remainder worries on a diagnosis and which recognizes extent existence: There is the coloring-matter remainder clearly, processing was performed for the aforementioned sample in which residual silver with diagnosis top trouble carried out appraisal method creation for 45 seconds like the above in the unexposed state, and the sample for residual silver evaluation was created. Evaluation of residual silver was performed by the following approach.

[0156] One drop is dropped at each five on the aforementioned residual silver evaluation film by using the 2.6×10^{-3} mol/l. water solution of a sodium sulfide as residual silver evaluation liquid. the silver sulfide which often wipes liquid and is generated after 15-hour neglect under ordinary temperature normal relative humidity after neglect for 3 minutes -- photographic-densitometer PDA-65 (product made from the Konica [stock]) -- using -- a spectrum -- the blue light transmission concentration of a part for the residual silver evaluation drop lower part and the part which is not dropped was measured with the interference filter of 436**10nm of filters, the difference was averaged, and it considered as the residual silver content.

[0157] It is shown that the residual silver concentration in the film after processing is so high that this difference is large.

[0158] The exam followed the Ath page of a sample film, and the Bth page. These obtained results are shown in Table 2.

[0159]

[Table 2]

試料 No.	フィル ム No.	染料		D B	写真性能			処理性		備 考
		例 示	添加量 (mg/m ²)		感度	カブリ	鮮銳性	残色性	残留銀	
1	I	A+B	500	-	100	0.02	A	D	0.12	比較
2	II	-	-	0.25	95	0.02	E	A	0.02	"
3	III	A+B	500	0.03	80	0.02	B	C	0.02	"
4	III	1-2	500	0.03	96	0.01	A	A	0.02	本発明
5	IV	1-2	500	0.02	98	0.01	A	A	0.02	"
6	V	1-2	500	0.02	100	0.01	A	A	0.01	"
7	IV	1-5	500	0.02	99	0.01	A	A	0.01	"
8	IV	1-3	100	0.02	98	0.01	B	A	0.02	"
9	IV	1-3	300	0.02	97	0.01	A	A	0.01	"
10	IV	1-3	500	0.02	96	0.01	A	A	0.01	"
11	IV	2-1	800	0.02	97	0.01	A	B	0.02	"
12	IV	3-3	500	0.02	98	0.01	A	A	0.01	"
13	IV	5-3	500	0.02	98	0.01	A	A	0.02	"
14	IV	6-2	500	0.02	95	0.01	A	A	0.01	"
15	IV	8-1	500	0.02	97	0.01	A	A	0.01	"
16	IV	10-4	500	0.02	96	0.01	A	A	0.01	"
17	IV	6'-4	500	0.02	97	0.01	A	A	0.01	"
18	IV	9'-1	500	0.02	97	0.01	A	A	0.02	"
19	IV	11-4	500	0.02	98	0.01	A	A	0.02	"
20	VI	1-5	300	0.01	102	0.01	A	A	0.01	"
21	VII	1-5	300	0.01	102	0.01	A	A	0.01	"
22	VII	1-5	300	0.01	105	0.01	A	A	0.01	"

[0160] As compared with the comparison sample, sample No.4-22 of this invention had little fogging, and sharp nature was excellent so that clearly from Table 2. Moreover, the trace of the contamination factor of the film after the development by remaining color nature, residual silver, etc. was not accepted, either.

[0161]

[Effect of the Invention] The silver halide photosensitive material for CRT photography which there is no generating of remaining color nature and residual silver, and has high definition by high sensitivity and high sharp nature by this invention even if it carries out quick processing was able to be obtained.

[Translation done.]

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(54)【発明の名称】 CRT撮影用ハロゲン化銀写真感光材料

(57)【要約】

【目的】 迅速処理しても残色性、残留銀の発生がなく、高感度、高鮮鋭性で高画質を有するCRT撮影用ハロゲン化銀写真感光材料の提供。

【構成】 (1) 透明支持体の一方の面(A面)に少なくとも1層のハロゲン化銀乳剤層と親水性コロイド層を有し、もう一方の面(B面)にハロゲン化銀乳剤層と該乳剤層より外側に染料の銀塩を含有した親水性コロイド層を少なくとも1層有することを特徴とするCRT撮影用ハロゲン化銀写真感光材料による。

用ハロゲン化銀写真感光材料により達成される。

【0010】以下、本発明を詳述する。

【0011】本発明に係るハロゲン化銀写真感光材料は、透明支持体の一方の側(A面)から露光し現像したとき、露光量が一方の面(A面)にカブリ濃度+1.10を与える露光量であった場合に、B面の濃度がカブリ+0.20以下であることが好ましく、特に好ましくは0.10以下である。

【0012】このような写真性能を得るには、A面からの露光に対しB面側が低感度となる構成で、例えばA面の乳剤よりも低感度の乳剤をB面に用いる方法、又はA面側に光吸収を多くする構成として、例えばA面の銀量を増量する方法又は染料をA面に用いる方法、或はA面に平板状粒子を用いる方法などが知られている。

【0013】本発明のハロゲン化銀写真感光材料においては、高感度面からの片面露光の際に、支持体を透過して低感度面へ到達する光の透過光量(クロスオーバー光)は、通常のX線撮影用両面感光材料よりも多いことが好ましい。

【0014】実技的には、用いるCRTの発光輝度光の透過率が12%~75%以下の範囲が好ましく、より好ましくは16%以上65%以下である。その理由はCRTの輝度光の透過率が多くなるほど鮮銳性の劣化を招くためである。

【0015】本発明のハロゲン化銀写真感光材料は、CRTに用いられる蛍光体の黄緑色発光に対応するようにオルソ分光増感されていることが好ましい。分光増感法としては例えば特開昭63-168642号に開示されている方法を用いることが出来る。

【0016】次に本発明に用いられる染料について説明する。

【0017】CRT撮影用ハロゲン化銀写真感光材料においては、特定の波長の光を吸収させて写真乳剤層を通過する際、散乱された光がフィルムホルダー表面から反射散乱されて再び乳剤層に入射し像様画像を形成する。この画像はいわゆるボケ画像のため鮮銳性を著しく劣化する。

【0018】本発明はこのハレーション光を吸収防止することにあって、B面のハロゲン化銀乳剤層の外側に着色層を設けることである。

【0019】本発明の上記目的のために染料は下記の条件を満足することが望ましい。

【0020】(1)染料は使用するCRTの発光領域に吸収を有すること

(2)染料は写真化学的に不活性で、写真特性に悪影響を与えないこと

(3)染料は処理過程で脱色又は溶解除去され処理後の感光材料に着色汚染を残さないことなどが挙げられる。

従来より染料層を設ける方法に関しては、染料が隣接するハロゲン化銀乳剤層に拡散し感度やコントラストなど

【特許請求の範囲】

【請求項1】 透明支持体の一方の面(A面)に少なくとも1層のハロゲン化銀乳剤層と親水性コロイド層を有し、もう一方の面(B面)にハロゲン化銀乳剤層と該乳剤層より外側に染料の銀塩を含有した親水性コロイド層を少なくとも1層有することを特徴とするCRT撮影用ハロゲン化銀写真感光材料。

【発明の詳細な説明】

【0001】

【産業上の利用分野】 本発明は、CRT(カソードレイチューブ)を光源として撮影するハロゲン化銀写真感光材料に関するもので、詳しくは高感度で、かつ画像の鮮銳性が優れ、迅速処理可能なCRT撮影用ハロゲン化銀写真感光材料に関するものである。

【0002】

【発明の背景】 CRT撮影用ハロゲン化銀写真感光材料は、医療用X線CTなどのCRT画像のハードコピーとしての透過画像用フィルムである。

【0003】近年、感光材料には益々迅速処理性が要求され、CRT用感光材料においてもその例外ではない。

【0004】感光材料の処理性を高めるひとつの手段として、例えばハロゲン化銀量を少なくし、かつ最高濃度を得るためにハロゲン化銀を小粒子化するなどが挙げられる。しかしながら該方法では感光度の大幅な低下を招き、その結果CRTの輝度を上げたり、露光時間を長くしたりするため著しく画像の劣化を伴う。

【0005】従って所望の感光度を得るために、やむを得ず粒径の大きいハロゲン化銀粒子を多量に用いる構成にせざるを得ないのが実情であった。

【0006】その結果、迅速処理にて定着が不充分となり、残留銀や残留ハイポ或は色素染料などによる残色汚染が発生する原因となっていた。

【0007】又、医療用感光材料として画像の鮮銳性を高めるために、片面のみに乳剤を塗布したフィルムがあるが、高感度、高濃度を維持するためには必然的に一定量以上のハロゲン化銀を必要とし、その結果、上述したと同様に、現像性、定着性、水洗性、或は乾燥性能などが低下し汚染を発生し易く画像の品質を損ねる結果となっていた。

【0008】

【発明の目的】 従って本発明の目的は、迅速現像処理しても残色性、残留銀の発生がなく高感度、高鮮銳性で高画質を有するCRT撮影用ハロゲン化銀写真感光材料を提供することである。

【0009】

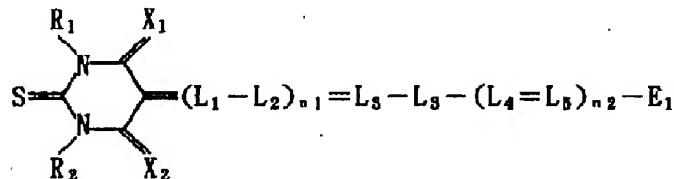
【発明の構成】 本発明の上記の目的は、透明支持体の一方の面(A面)に少なくとも1層のハロゲン化銀乳剤層と親水性コロイド層を有し、もう一方の面(B面)にハロゲン化銀乳剤層と該乳剤層より外側に染料の銀塩を含有した親水性コロイド層を少なくとも1層有するCRT撮影

の低下をもたらすことから染料の拡散防止方法が知られており、例えば水溶性染料の固定化技術として高分子のモルダントを用いる方法が知られている。

【0021】しかしながら、該方法では最近のように全処理時間が60秒以下であるような迅速処理においては、処理後の残色汚染が生じ易い欠点を有している。

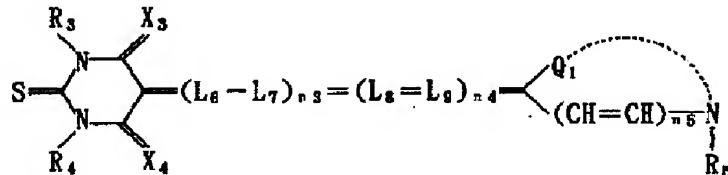
【0022】本発明における染料の銀塩とは、染料と銀イオンとの反応により形成される銀塩及び銀錯体を指し、染料とは可視スペクトル域の(380nm~700nm)に吸収*

一般式 [1]



【0026】式中、R₁、R₂は水素原子、アルキル基、アルケニル基、アリール基、複素環基を表し、X₁、X₂は酸素原子、イオウ原子を表す。L₁～L₅はメチン基を表し、n₁、n₂は0～2の整数を表す。またE₁は酸性の核※

一般式 [2]

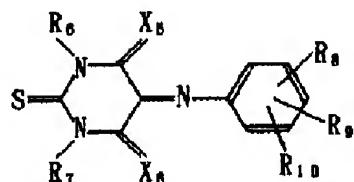


【0028】式中、R₃、R₄は一般式[1]におけるR₁、R₂と同義であり、X₃、X₄は一般式[6]におけるX₁、X₂と同義である。L₆～L₉はメチン基を表し、n₃～n₅は0～2の整数を表す。R₅はアルキル基、アルケニル基を表し、Q₁は5員または6員の複素環を形成するのに必要な非金属原子群を表す。

【0029】

【化3】

一般式 [3]



*を有する有機化合物を指す。

【0023】以下、本発明において用いられる銀塩を形成し得る好ましい染料を挙げるが、本発明はこれらに限定されるものではない。

【0024】上記染料は下記一般式[1]～[5]で表される染料を挙げることができる。

【0025】

【化1】

※を有する基を表す。

【0027】

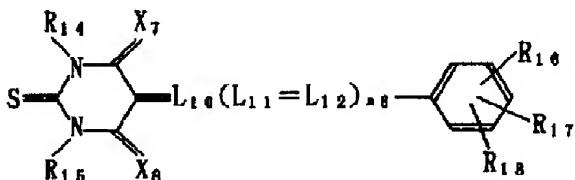
【化2】

【0030】式中、R₆、R₇は一般式[1]におけるR₁、R₂と同義であり、X₅、X₆は一般式[1]におけるX₁、X₂と同義である。R₈～R₁₀は水素原子、アルキル基、アルケニル基、アリール基、複素環基、ハロゲン原子、シアノ基、スルホ基、-COR₁₁、-CON(R₁₁)(R₁₂)、-N(R₁₁)(R₁₂)、-OR₁₁、-SOR₁₁、-SO₂R₁₁、-SO₂N(R₁₁)(R₁₂)、-N(R₁₁)COR₁₂、-N(R₁₁)SO₂R₁₂、-N(R₁₁)CON(R₁₂)(R₁₃)、-SR₁₁、-COOR₁₁を表し、R₁₁～R₁₃は水素原子、アルキル基、アルケニル基、アリール基、複素環基を表す。

【0031】

【化4】

5
一般式 [4]

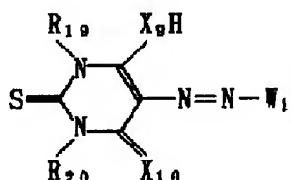


【0032】式中、R₁₄、R₁₅は一般式〔1〕におけるR₁、R₂と同義であり、X₇、X₈は一般式〔1〕におけるX₁、X₂と同義である。L₁₀～L₁₂はメチル基を表し、n₆は0～6の整数表す。R₁₆～R₁₈は一般式〔3〕におけるR₈～R₁₀と同義である。

【0033】

【化5】

一般式 [5]



【0034】式中、R₁₉、R₂₀は一般式〔1〕におけるR₁、R₂と同義であり、X₉、X₁₀は一般式〔1〕におけるX₁、X₂と同義である。W₁はアリール基又は複素環基を表す。

【0035】一般式〔1〕においてR₁～R₂で表されるアルキル基としては、例えばメチル基、エチル基、プロピル基、イソプロピル基、n-ブチル基、tert-ブチル基、シクロヘキシル基、シクロヘキシル基などが挙げられる。これらのアルキル基は更にヒドロキシ基、シアノ基、スルホ基、カルボキシル基、ハロゲン原子(例えばフッ素原子、塩素原子、臭素原子など)、アルコキシ基(例えばメトキシ基、エトキシ基など)、アリールオキシ基(例えばフェノキシ基、4-スルホフェノキシ基、2,4-ジスルホフェノキシ基など)、アリール基(例えばフェニル基、4-スルホフェニル基、2,5-ジスルホフェニル基など)、アルコキシカルボニル基(例えばメトキシカルボニル基、エトキシカルボニル基など)、アリールオキシカルボニル基(例えばフェノキシカルボニル基など)によって置換されていてもよい。

【0036】R₁、R₂で表されるアリール基は、例えばフェニル基、ナフチル基が挙げられる。これらの基はR₁、R₂で表したアルキル基及び置換アルキル基と同様の基によって置換していくてもよい。

【0037】R₁、R₂で表される複素環基としては、例えばピリジル基、チアゾリン基、オキサゾリン基、イミダゾリン基、フリル基、ピロリ基、ピラジニル基、ピ

10 リミジニル基、ピリダジニル基、ブリニル基、セレナゾリル基、スルホラニル基、ピペリジニル基、ピラゾリル基、テトラゾリル基等が挙げられる。

【0038】これらの基はR₁、R₂で表される基及びアルキル基の置換基として表したものと同様の基によって置換することができる。

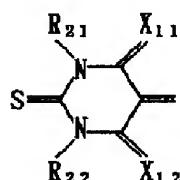
【0039】R₁、R₂で表されるアルケニル基としては例えばビニル基、アリル基等が挙げられる。これらの基はR₁、R₂で表されるアルキル基、及びアルキル基の置換基として表した置換基と同様な基によって置換することができる。

20 【0040】一般式〔1〕においてE₁で示される酸性の核を有する基としては、例えば、特開昭61-281235号公報の11頁20行目から14頁15行目までに記載された骨核を有する基、及び下記式1～4で表される基を挙げることができる。

【0041】

【化6】

式 1

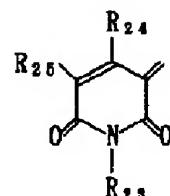


【0042】式中、R₂₁、R₂₂は前記一般式〔1〕のR₁、R₂と同義であるがR₂₁はR₂₂と同一ではない。またX₁₁、X₁₂は一般式〔1〕におけるX₁、X₂と同義である。

【0043】

【化7】

式 2

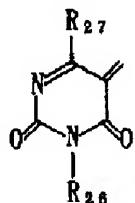


【0044】式中、R₂₃は前記一般式〔1〕におけるR₁、R₂と同義でR₂₄、R₂₅は前記一般式〔3〕におけるR₈～R₁₀と同義である。

【0045】

【化8】

式3

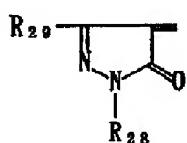


【0046】式中、R₂₆ は前記一般式〔1〕におけるR₁、R₂と同義でR₂₇ は前記一般式〔3〕におけるR₈～R₁₀と同義である。

【0047】

【化9】

式4



【0048】式中、R₂₈ は前記一般式〔1〕におけるR₁、R₂と同義であり、R₂₉ はアルキル基、アリール基、アルケニル基、複素環基、シアノ基、-COR₃₀、-CON(R₃₀)(R₃₁)、-N(R₃₀)(R₃₁)、-OR₃₀、-SOR₃₀、-SO₂R₃₀、-SO₂N(R₃₀)(R₃₁)、-NR₃₀COR₃₁、-N(R₃₀)SO₂R₃₁、-N(R₃₀)CON(R₃₁)(R₃₂)、-SR₃₀、-COOR₃₀を表す。

【0049】R₃₀～R₃₁ は前記一般式〔3〕におけるR₁₁～R₁₃と同義である。

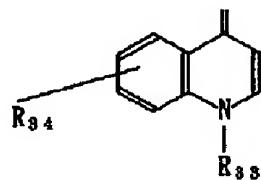
【0050】上記のアルキル基、アルケニル基、アリ-

ル基、及び複素環基としては先のR₁、R₂の説明で示したものと同様の基が挙げられる。

【0051】以上の説明において、Eで表される酸性の核を有する基をケト型で表したが、互変異性によりエノール型を取り得ることは化学的に考えて明らかである。

【0052】一般式〔2〕においてQ₁により形成される5員または6員の複素環としては例えば、特開昭61-282832号の23～26頁に記載された複素環及び下記の式5で表されるものが挙げられる。

10 【0053】

【化10】
式5

20 【0054】式中、R₃₃ は前記一般式〔1〕におけるR₁及びR₂と同義であり、R₃₄ は前記一般式〔3〕におけるR₈～R₁₀と同義である。

【0055】一般式〔5〕において、W₁で表されるアリール基とは、例えばフェニル基を挙げることができ複素環基としてはピリジル基、チアゾリル基、オキサゾリル基を挙げることができ、これらの基は置換基を有してもよい。

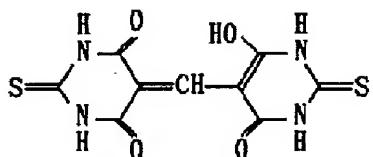
【0056】以下、一般式〔1〕、〔2〕、〔3〕、〔4〕及び〔5〕で表される化合物の代表的具体例を示すが本発明はこれらに限定されるものではない。

30 【0057】

【化11】

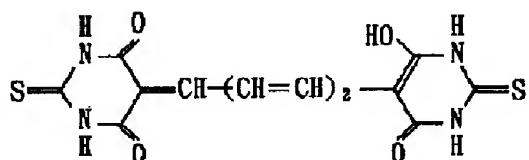
(6)

特開平 5-257217

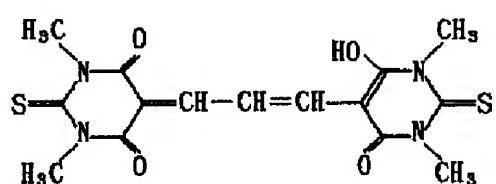
9
1 - 1

10

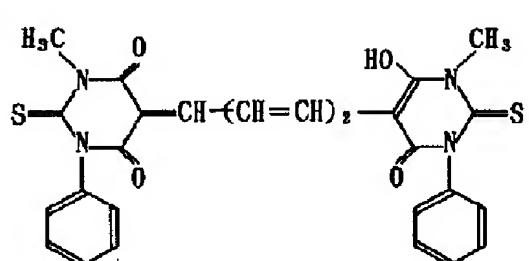
1 - 2



1 - 3



1 - 4



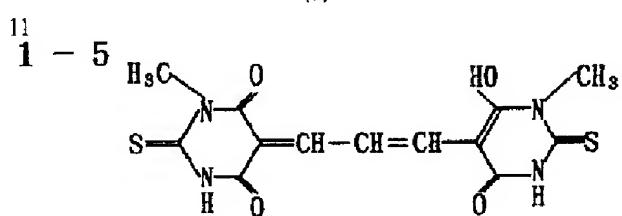
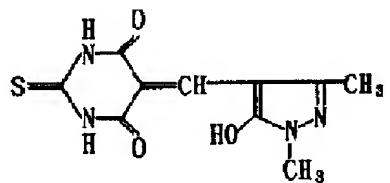
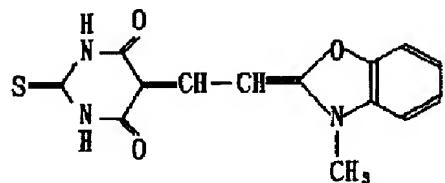
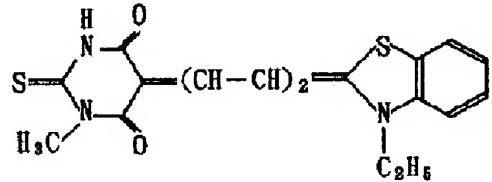
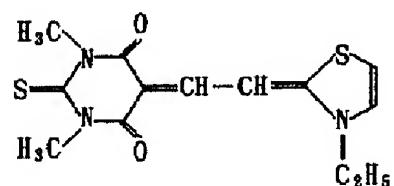
【0058】

【化12】

(7)

特開平5-257217

12

**1 - 6****2 - 1****2 - 2****2 - 3**

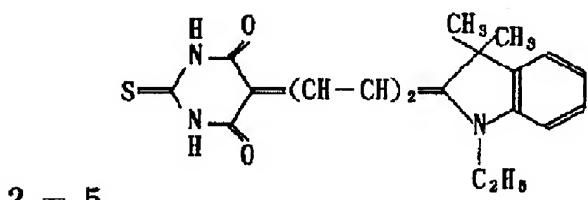
【0059】

【化13】

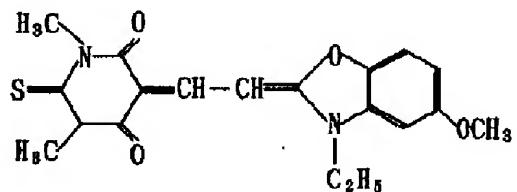
(8)

特開平5-257217

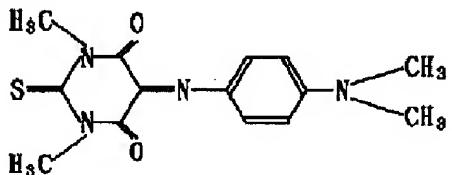
14

2 - 4¹³

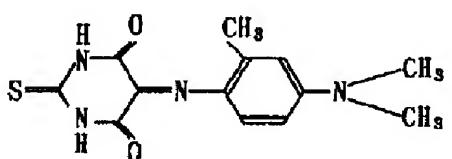
2 - 5



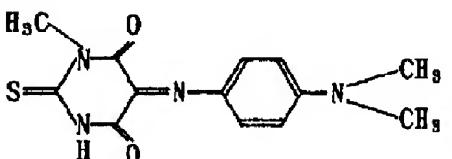
3 - 1



3 - 2



3 - 3

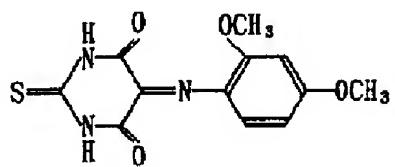


【0060】

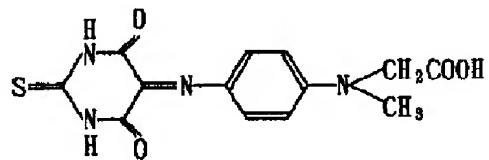
【化14】

3 - 15

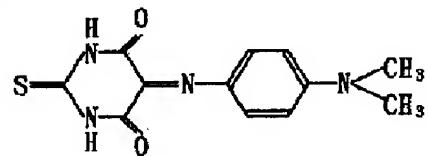
(9)



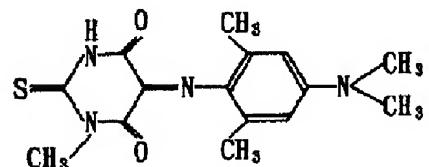
3 - 5



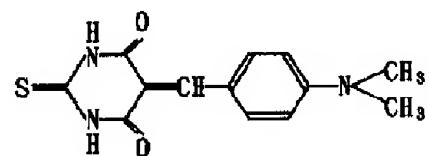
3 - 6



3 - 7



4 - 1



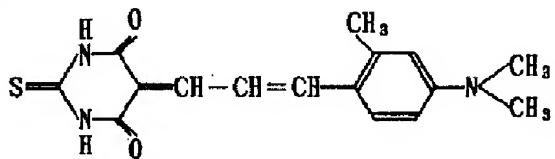
【0061】

【化15】

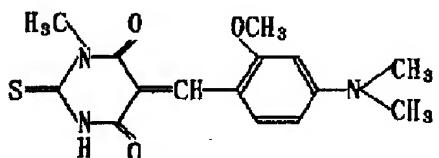
(10)

特開平5-257217

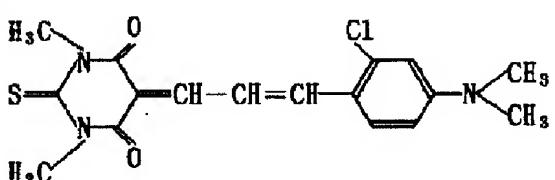
18

¹⁷
4 - 2

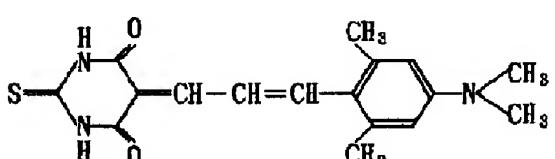
4 - 3



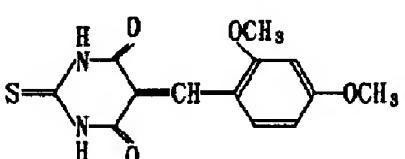
4 - 4



4 - 5



4 - 6



【0062】

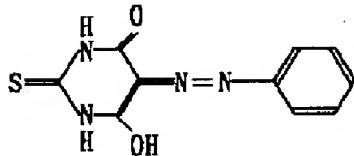
【化16】

(11)

特開平5-257217

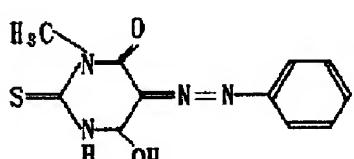
5-1

19

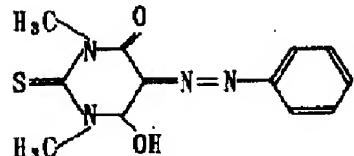


5-2

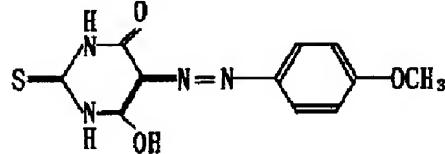
10



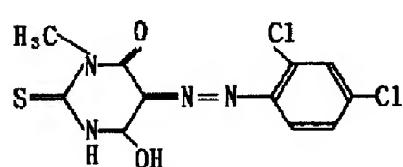
5-3



5-4



5-5



【0063】なお上記の染料以外に、本発明に好ましく用いられる染料としては本発明の出願人と同一人による特願平3-189488号明細書第14頁～第20頁に記載の染料を好ましく用いることができる。

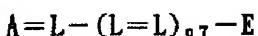
【0064】さらに本発明で用いることができる染料としては、上記のほかに下記一般式〔1'〕～〔5'〕で表される染料を挙げることができる。

【0065】

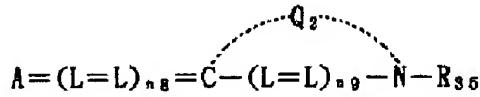
【化17】

(11) 一般式〔1'〕

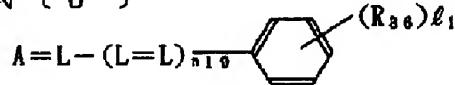
20



一般式〔2'〕



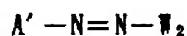
一般式〔3'〕



一般式〔4'〕



一般式〔5'〕

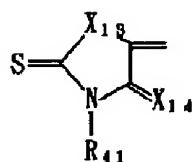
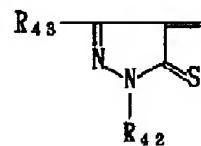
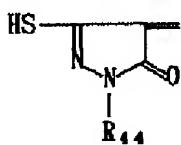
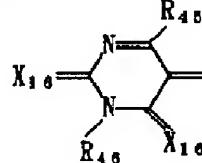
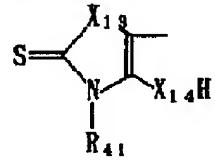
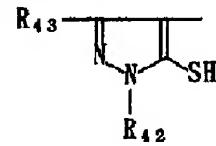
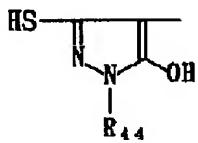
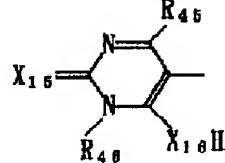


【0066】上記一般式〔1'〕～一般式〔5'〕において R_{38} はアルキル基、アルケニル基を表し、 R_{36} 及び R_{37} はアルキル基、アルケニル基、アリール基、複素環基、ハロゲン原子、シアノ基、スルホ基、 $-COR_{38}$ 、 $-CON(R_{38})(R_{39})$ 、 $-N(R_{38})(R_{39})$ 、 $-OR_{38}$ 、 $-SOR_{38}$ 、 $-SO_2R_{38}$ 、 $-SO_2N(R_{38})(R_{39})$ 、 $-N(R_{38})COR_{38}$ 或は、 $-N(R_{38})SO_2R_{39}$ 、 $-N(R_{38})CON(R_{39})(R_{40})$ 、 $-SR_{38}$ 、 $-COOR_{38}$ を表し $R_{38} \sim R_{40}$ は水素原子、アルキル基、アルケニル基、アリール基、複素環基を表す。

【0067】 A は下記一般式〔A₁〕～〔A₄〕で表される基を表し、 A' は下記一般式〔A'₁〕～〔A'₄〕で表される基を表す。

【0068】

【化18】

21
一般式 [A₁]22
一般式 [A₂]一般式 [A₃]一般式 [A₄]一般式 [A'₁]一般式 [A'₂]一般式 [A'₃]一般式 [A'₄]

【0069】一般式[A₁]～[A₄]及び一般式[A'₁]～[A'₄]においてR₄₁、R₄₂、R₄₃及びR₄₆は水素原子、アルキル基、アルケニル基、アリール基、複素環基を表しR₄₅はアルキル基、アルケニル基、アリール基、複素環基、シアノ基、スルホ基、-COR₄₇、-CON(R₄₇)(R₄₈)、-N(R₄₇)(R₄₈)、-OR₄₇、-SOR₄₇、-SO₂R₄₇、-SO₂N(R₄₇)(R₄₈)、-N(R₄₇)COR₄₈、-N(R₄₇)SO₂R₄₈、-N(R₄₇)CON(R₄₈)(R₄₉)、-SR₄₇、-COOR₄₇を表し、R₄₇～R₄₉は水素原子、アルキル基、アルケニル基、アリール基、複素環基を表す。R₅₀はR₃₀及びR₃₇と同義である。

【0070】Lはメチン基を表しEは酸性の核を有する基を表す。Q₂は複素環を形成するのに必要な非金属原子群を表す。W₂はアリール基、複素環基を表す。X₁₃は酸素原子、イオウ原子、セレン原子、=N-R₅₀を表す。R₅₀はR₄₁と同義である。

【0071】X₁₄、X₁₅及びX₁₆は酸素原子、硫黄原子を表す。n₁、n₂は0～3、n₃、n₄は0～2の整数を表し、l₁、l₂は0～3を表す。

【0072】上記一般式[1']～[5']においてR₃₀～R₅₀で表されるアルキル基としては例えばメチル基、エチル基、プロピル基、イソプロピル基、n-ブチル

30 基、tert-ブチル基、シクロペンチル基、シクロヘキシル基などが挙げられる。これらのアルキル基にはヒドロキシ基、シアノ基、スルホ基、カルボキシル基、ハロゲン原子(例えばフッ素原子、塩素原子、臭素原子など)、アルコキシ基(例えばメトキシ基、エトキシ基など)、アリールオキシ基(例えばフェノキシ基、4-スルホフェノキシ基、2,4-ジスルホフェノキシ基など)、アリール基(例えばフェニル基、4-スルホフェニル基、2,5ジスルホフェニル基など)、アルコキシカルボニル基(例えばメトキシカルボニル基、エトキシカルボニル基など)、アリールオキシカルボニル基(例えばフェノキシカルボニル基など)によつて置換されていてもよい。

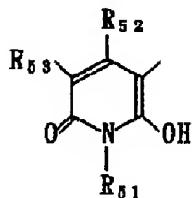
【0073】R₃₀～R₅₀及びWで表されるアリール基としては、例えばフェニル基、ナフチル基が挙げられる。これらの基はR₁～R₁₆で表されるアルキル基、及びアルキル基の置換基として表した置換基と同様の基によって置換することができる。

【0074】R₃₀～R₅₀及びWで表される複素環基としては、例えばピリジン基、チアゾリル基、オキサゾリル基、イミダゾリル基、フリル基、ピロリル基、ピラジニル基、ピリミジル基、ピリダジニル基、プリニル基、セ

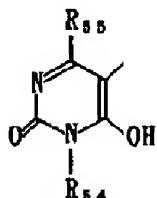
レナゾリル基、スルホラニル基、ピペリジニル基、ピラゾリル基、テトラゾリル基などが挙げられる。これらの基はR₅₃～R₅₆で表されるアルキル基及びアルキル基の置換基として表した置換基と同様の基によって置換することができる。

【0075】R₅₃～R₅₆で表されるアルケニル基としては、例えはビニル基、アリル基などが挙げられ、これらの基はR₅₃～R₅₆で表されるアルキル基及びアルキル基の置換基として表した置換基と同様の基によって置換する*

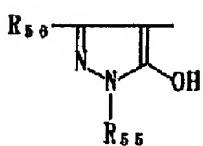
一般式 [B-I]



一般式 [B-II]



一般式 [B-III]



【0078】式中、R₅₁はR₄₁と同義であり、R₅₂、R₅₃は水素原子及び先にR₅₀として示した基を表す。R₅₄はR₄₀と同義でありR₅₅は水素原子及び先のR₅₀として示した基を表す。R₅₆はR₄₂と同義であり、R₅₆はR₄₃と同義である。

【0079】一般式[2']においてQ₂により形成される複素環としては、例えは特開昭61-282832号公報の23～26頁に記載された複素環及び下記一般式[B-IV]で表される複素環を挙げることができる。

【0080】

【化20】

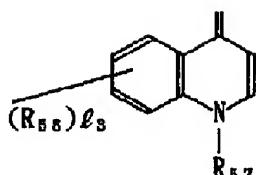
* ことができる。

【0076】一般式[1']においてEで表される酸性の核を有する基としては、例えは特開昭61-28123号公報の第11頁20行目から第14頁15行目までに記載された骨格を有する基及び一般式[A'-1]～[A'-4]に示された核を有する基及び下記の一般式[B-I]、[B-II]及び[B-III]で表される基を挙げることができる。

【0077】

【化19】

一般式 [B-IV]



【0081】式中、R₅₇はR₄₄と同義であり、R₅₈はR₃₉と同義である。I₁は0～3の整数である。

【0082】以下に一般式[1']～一般式[5']で表される化合物の代表的具体例を示すが本発明はこれらのみに限定されるものではない。

(14)

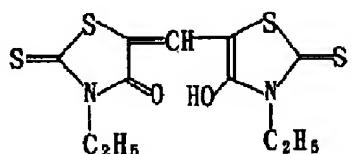
25

特開平5-257217

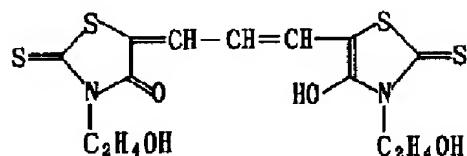
26

【化21】

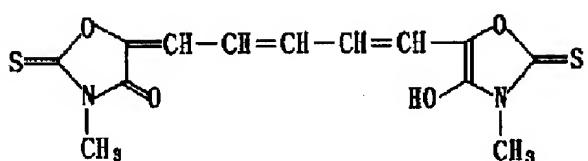
1'-1



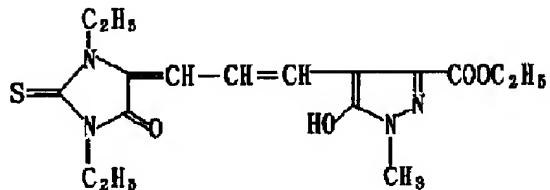
1'-2



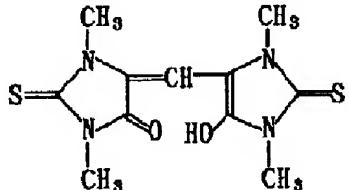
1'-3



1'-4



1'-5

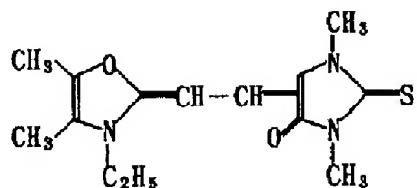


【0084】

【化22】

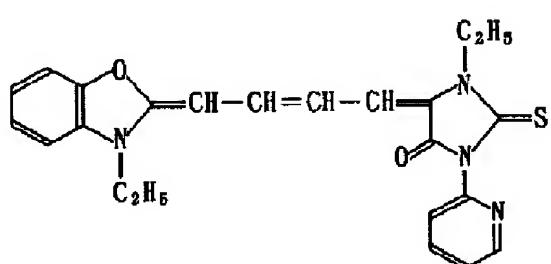
(15)

特開平5-257217

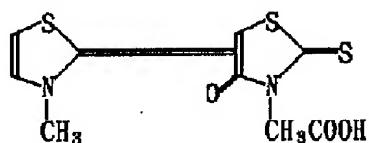
2'-1²⁷

28

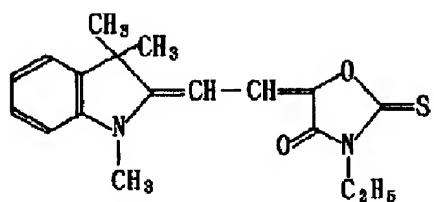
2'-2



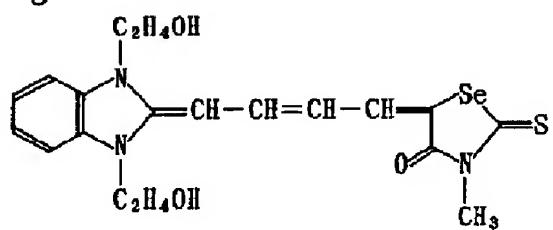
2'-3



2'-4



2'-5



【0085】

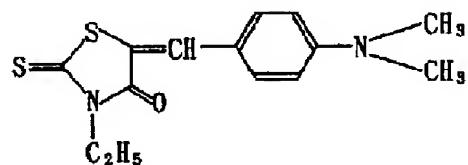
【化23】

(16)

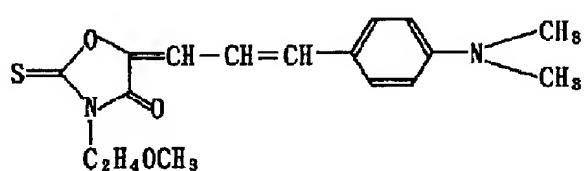
特開平5-257217

3'-²⁹
1

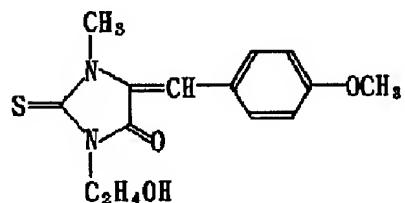
30



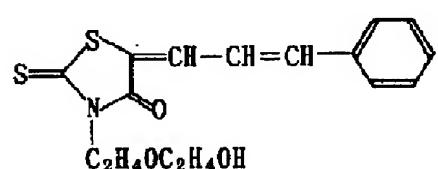
3'-2



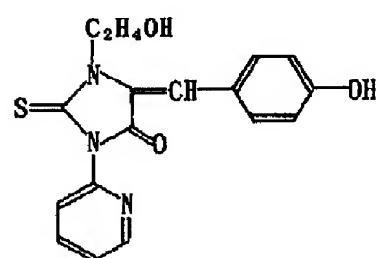
3'-3



3'-4



3'-5



【0086】

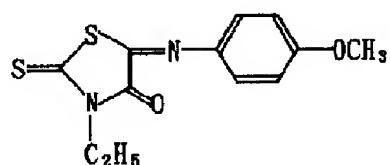
【化24】

特開平 5-257217

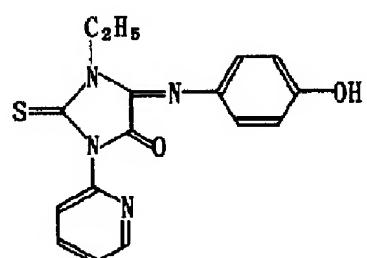
32

(17)

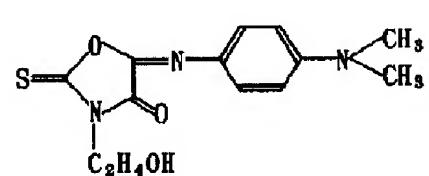
4' - 1³¹



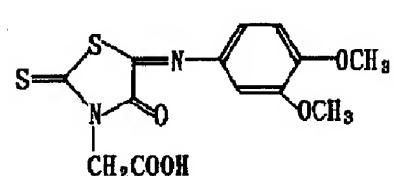
4' - 2



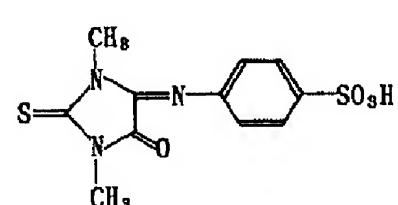
4' - 3



4' - 4

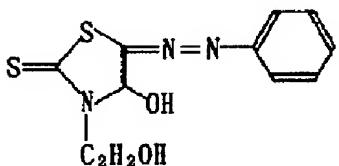


4' - 5

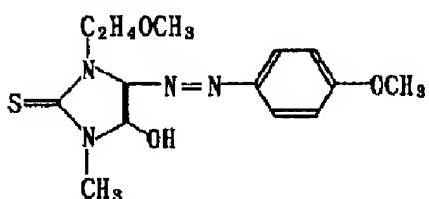


【0087】

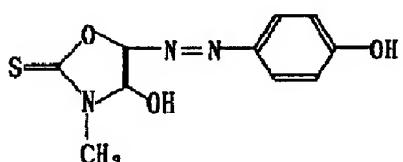
【化25】

³³
5'-1

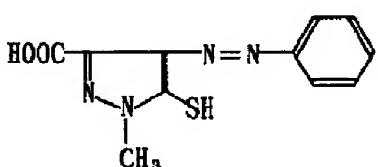
5'-2



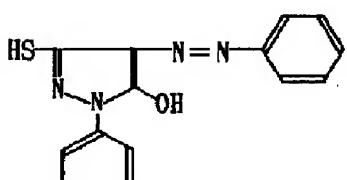
5'-3



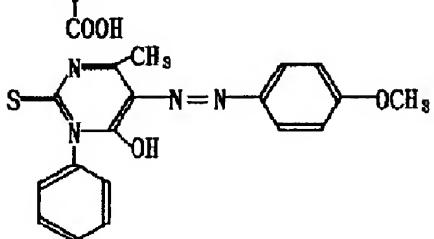
5'-4



5'-5



5'-6



【0088】なお上記の染料以外に、本発明に好ましく用いられる染料としては本発明の出願人と同一人による特願平3-189488号明細書第26頁～第34頁に記載の染料を好ましく用いることができる。

【0089】更に本発明に好ましく用いることができる染料としては、下記一般式〔6〕で表される染料が挙げられる。

【0090】

一般式〔6〕 (Dye)_{n₁} [-(J)n₂-Sal]_{n₃}
式中、Dyeはメチン染料構造を有する原子群を表し、Jは炭素原子、窒素原子、酸素原子、硫黄原子から選ばれる原子または原子団を骨核とする2価の連結基を表し、Salは銀イオンと難溶性の塩を形成する基を表し、n₁

は1または2、n₂は0または1を、n₃は1～4を表す。

40 【0091】上記の一般式〔6〕においてDyeで示される基はメチン染料構造を有する原子群を表し、例えばシアニン、メロシアニン、メロスチリル、スチリル、オキソノール、トリアリールメタンなどのメチン鎖が共役二重結合されている染料構造を有する基である。これらの染料の具体例としては例えば特開昭63-202665号、ソビエト国特許653,257号に記載のシアニン染料、特開昭52-29727号、同52-60825号、同52-135335号、同56-27146号、同56-29226号、同59-10944号、同59-15934号、同59-111847号、同63-34539号、米国特許2,944,896号、同3,148,187号記載のメロシアニン染料、特開昭52-211041

号、同59-211042号、同60-135936号、同60-135937号、同61-204630号、同61-205934号、同62-56958号、同62-70830号、同62-92949号、同62-185758号などに記載のメロスチリル染料、特開昭50-145125号、同55-33103号、同55-120660号、同55-161233号、同62-185755号、同63-139949号、同63-231445号、同63-264745号、米国特許4,187,275号、英國特許1,521083号、ベルギー国特許869,677号などに記載のオキソノール染料、特開昭59-55437号、同59-228250号、米国特許4,115,126号、同4,359,574号などに記載のトリアリールメタン染料が挙げられる。

【0092】さらにT.H.James編 "The Theory of the Photographic process" 第4版、Macmillan社刊(1977年)、F.M.Hamer著 "Heterocyclic Compound Cyanin Dyes and related Compound" John Wiley & Sons(New York London)1964年刊、D.M.Sturmer著 "The Chemistry of Heterocyclic Compounds" ed.A.Weiss berger and E.C.Taylor, 1977年刊、"The Chemistry of Synthetic Dyes" Academic press (New York London) Vol.11, 1952年刊、同Vol.IV, 1971年刊などの成書に記載されているものから選択される。

【0093】式中のJは炭素原子、窒素原子、酸素原子、硫黄原子から選ばれる原子または原子団を骨格とする2価の連結基を表す。好ましい基はアルキレン基(例えばメチレン、エチレン、プロピレン、ベンチレン基など)、アリレン基(例えばフェニレン基など)、アルケニレン基(例えばアリレン基など)、スルホニル基、スルフィニル基、エーテル基、チオエーテル基、カルボニル基、-N(R₆)基、(R₆は水素原子、置換または非置換のアルキル基、置換または非置換のアリール基)、-N=基、複素環2価基(例えばトリアジン-2,4-ジイル基、ビリミジン-2,4-ジイル基、チアゾール-2,4-ジイル基、ベンゾオキサゾール-2,5-ジイル基など)を1つまたはそれ以上組み合わせて構成される炭素数20以下の2価の連結基で

あり置換基を有していてもよい。

【0094】置換基としては一般的なものが挙げられ、ハロゲン原子(例えばフッソ原子、塩素原子、臭素原子など)、アルキル基(例えばメチル、エチル、イソプロピル、ブチル基など)、アラルキル基(例えばベンジル、フェネチル基など)アルコキシ基(例えばメトキシ、エトキシなど)、アルコキシカルボニル基(例えばエトキシカルボニル基など)、アルキルチオ基、ヒドロキシ基、カルボキシ基、スルホ基、スルホニル基(例えばメタンスルホニル基、p-トルエンスルホニル基など)、カルバモイル基(例えばN-メチルカルバモイル基、モルホリノカルボニルスルファモイル基など)、アシリル基(例えばアセチル基、ベンゾイル基など)、アシリアミド基(例えばアセトアミド基など)、スルホニアミド基(例えばメタンスリホニアミド基、ブタンスルホニアミド基など)、シアノ基、アミノ基(例えばエチルアミノ基、ジメチルアミノ基など)、ウレイド基などの任意の基が選択される。

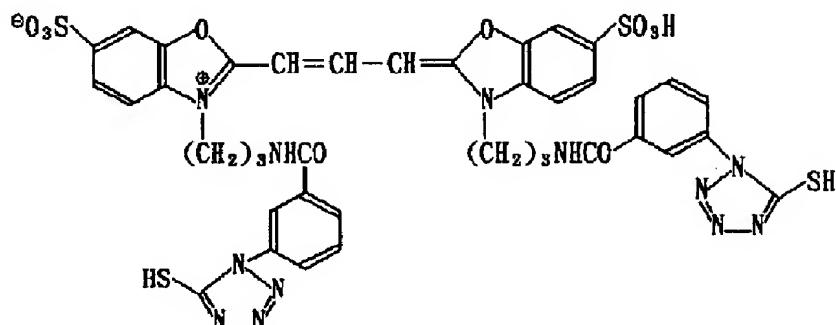
【0095】式中のn₁は1または2を、n₂は0又は1を、n₃は1、2、3又は4を表す。

【0096】Salは銀イオンと難溶性の塩を形成する基を表支持体、例えばメルカプト基、アセチレン基、チオカルボニル基、チオアミド基、チオウレタン基、チオウレイド基(例えば3-エチルチオウレイド基、3-フェニルチオウレイド基など)、或は少なくとも1個の窒素原子を環内に含む飽和又は不飽和の5~7員の複素環残基が挙げられる。好ましい基としては特開平2-97937号記載の一般式(VIII)、(IX)で示される基又は特開平2-225476記載の一般式(II)~(VI)で示される基が挙げられる。

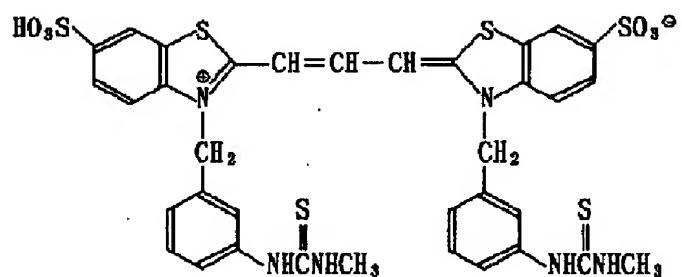
【0097】以下、本発明の一般式〔6〕で表される染料の具体的化合物を示すが本発明はこれらに限定されるものではない。

【0098】

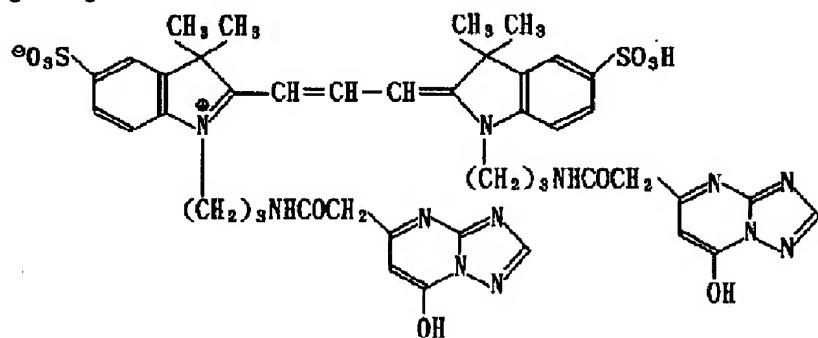
【化26】

6 - 1³⁷

6 - 2

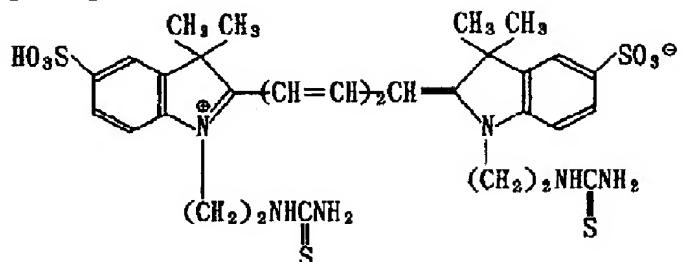


6 - 3

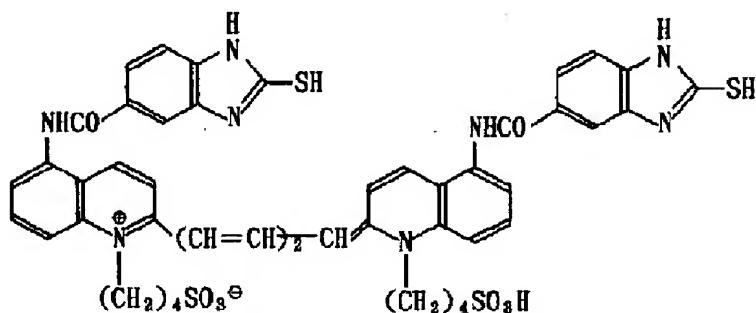


【0099】

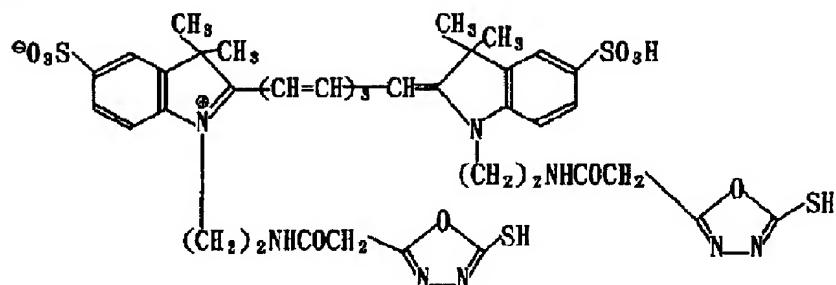
【化27】

6 - 4³⁹

6 - 5



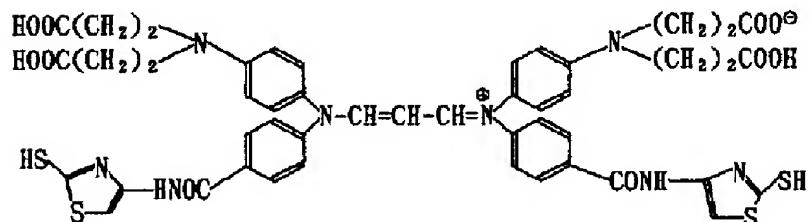
6 - 6



【0100】

6 - 7

* * 【化28】



【0101】なお上記の染料以外に、本発明によましく用いられる染料としては本発明の出願人と同一人による特願平3-189488号明細書第38頁～第39頁に記載の染料をよましく用いることができる。

【0102】本発明に係るメチン染料は予めSalで示した難溶性銀塩形成基を置換した中間体原料から染料化する方法、Dyeで示されるメチン染料構造部分とSal部分とを結合する方法のいずれでも良く、任意に選択合成する

ことができる。

【0103】Sal基の導入は種々の公知の結合反応を利用することができます。例えばビニル基やカルボニル基などの不飽和基への付加反応、アミノ基やヒドロキシ基などの活性水素置換基と酸誘導体や、ハロゲン誘導体との置換反応によって行なうことができる。これらの反応を行うに際しては、日本化学会編“新実験化学講座14”有機化学の合成と反応、I～V巻、(丸善)1962年刊、“Orga

nic Reactions" Vol. 1, 3, 12 John Wiley & Sons (New York London)、 "The Chemistry of functional Groups" John Wiley & Sons (New York London)、 "Advanced Organic Chemistry" L. F. Fieser and M. Fieser, (丸善) 1962年刊などの多くの成書を参考にすることができる。

【0104】本発明の上記の染料は、可溶性銀塩水溶液と反応させて難溶性の銀塩とし、これをハロゲン化銀感光材料中に分散添加する。

【0105】次に本発明に於ける感光材料のB面の親水性コロイド層中に上記の染料銀塩を含有せしめる場合、染料銀塩の付き量は0.01~2.0 g/m²が好ましく、特に0.05~1.0 g/m²が好ましい。親水性コロイド層のゼラチン付き量は0.3~1.5 g/m²が好ましく0.5~1.0 g/m²が好ましい。

【0106】なお、本発明のハロゲン化銀写真感光材料には、上記の染料銀塩の他に公知の染料を併用含有した親水性コロイドであってもよい。

【0107】本発明のハロゲン化銀写真感光材料に用いられる乳剤は、公知の方法で製造できる。例えばリサー・ディスクロージャー(R D)No. 17643(1978年12月)・22~23頁の1・乳剤製造法(Emulsion Preparation and types)及び同(R D)No. 18716(1979年11月)・648頁に記載の方法で調製することができる。

【0108】本発明に係るハロゲン化銀写真感光材料の乳剤は、例えば、T. H. James著 "The theory of the photographic process" 第4版、Macmillan社刊(1977年)38~104頁に記載の方法、C. F. Dauffin著「写真乳剤化学」「Photographic Emulsion Chemistry」、Focal press社刊(1966年)、P. Glafkides著「写真の物理と化学」「Chimie et physique photographique」Paul Montel 社刊(1967年)、V. L. Zelikman 他著「写真乳剤の製造と塗布」「Making and Coating photographic Emulsion」Focal press 社刊(1964年)などに記載の方法により調製される。

【0109】即ち中性法、酸性法、アンモニア法などの溶液条件にて順混合法、逆混合法、ダブルジェット法、コントロールド・ダブルジェット法などの混合条件、コンバージョン法、コア/シェル法などの粒子調製条件及びこれらの組合せ法を用いて製造することができる。好ましい例としては、沃化銀を粒子内部に局在させた単分散乳剤が挙げられる。

【0110】ここで単分散とは、95%以上の粒子が数平均粒径の±40%以内のサイズに入る分散系である。ここで数平均粒径とは、粒子の投影面積径の数平均直径である。本発明に用いられるハロゲン化銀粒子の内部構造は任意であるが、ハロゲン化銀組成の異なるコアシェル構造のものが好ましい。

【0111】シェルは、沃化銀、塩沃化銀、塩臭化銀、臭化銀、塩化銀等のハロゲン化銀によって被覆することにより形成される。好ましくは外表面から0.01 μm

以上、特に0.01~0.5 μmの厚さのシェル部分が沃化銀を10モル%以下を含む沃臭化銀で、沃化銀が5モル%以下の沃臭化銀で形成される。

【0112】種晶を使う場合には、種晶のみに少なくとも20%以上の臭化銀を形成し、この後シェル層で被覆してもよい。或いは種晶の沃化銀量を0とするかもしくは10モル%以下の範囲内とし、種晶を成長させる工程で粒子内部に少なくとも20%以上の沃化銀を形成させて、この後シェル層で被覆してもよい。

10 【0113】また20%以上の高濃度の沃化銀が局在化した局在化部分を有するハロゲン化銀粒子が好ましく使用できる。このような20%以上の高濃度沃化銀局在化部分は、粒子の外表面から0.01 μm以上離れた部分に局在部分が存在することが好ましい。

【0114】また局在化部分は、粒子内部にて層状に存在してもよく、コアシェル構造をとって、そのコア全体が局在化部分となっていてもよい。この場合外表面から0.01 μm以上厚さのシェル部分を除く粒子コア部の一部ないし全部が20モル%以上の沃化銀濃度の局在化部分であることが好ましい。局在化部分の沃化銀は、その濃度が30~40モル%であることがより好ましい。

【0115】本発明のハロゲン化銀写真感光材料の乳剤には平板状ハロゲン化銀粒子が好ましく挙げられる。

【0116】平板状ハロゲン化銀粒子の平均粒径は0.2~2.5 μmが好ましく、特に好ましくは0.5~2.0 μmである。平板状ハロゲン化銀乳剤は、粒子直径/厚さ(アスペクト比と呼ぶ)の平均値(平均アスペクト比と呼ぶ)が2以上であり、好ましくは3以上であり、特に好ましくは5~10である。

30 【0117】また平板状ハロゲン化銀乳剤の平均厚さは0.4 μm以下が好ましく、より好ましくは0.3 μm以下、特に好ましくは0.05~0.25 μmである。

【0118】平板状ハロゲン化銀乳剤は単分散性であるものが好ましく用いられ、平均粒径を中心にして±20%の粒径範囲に含まれるハロゲン化銀粒子が50重量%以上のものが特に好ましく用いられる。

40 【0119】平板状ハロゲン化銀乳剤は、塩化銀、臭化銀、塩沃化銀、塩臭化銀、沃臭化銀、塩沃臭化銀などでハロゲン化銀組成は任意であるが、高感度という点からは沃塩臭化銀が好ましく、この場合の平均沃化銀含有率は0~4.0モル%であって、特に好ましくは0.2~3.0モル%で平均塩化銀含有率は0~5モル%である。

【0120】又、平板状ハロゲン化銀乳剤は、ハロゲン化銀組成が粒子内で均一であってもよく、沃化銀が局在したものであってもよいが、中心部に局在したものが好ましく用いられる。

【0121】平板状ハロゲン化銀乳剤の製造方法は、特開昭58-113926号、同58-113927号、同58-113934号、同62-1855号、ヨーロッパ特許219,849号、同219,850号等を参考にすることもできる。

【0122】又、単分散性の平板状ハロゲン化銀乳剤の製造方法として、特開昭61-6643号を参考にすることができる。

【0123】高アスペクト比を持つ平板状の沃臭化銀乳剤の製造方法としては、 pBr が2以下に保たれたゼラチン水溶液に硝酸銀水溶液又は硝酸銀水溶液とハロゲン化物水溶液を同時に添加して種晶を発生させ、次にダブルジェット法により成長させることによって得ることができる。

【0124】平板状ハロゲン化銀粒子の大きさは、粒子形成時の温度、銀塩及びハロゲン化物水溶液の添加速度によってコントロールできる。

【0125】平板状ハロゲン化銀乳剤の平均沃化銀含有率は、添加するハロゲン化物水溶液の組成、すなわち臭化物と沃化物の比を変えることによりコントロールすることができる。

【0126】又、平板状ハロゲン化銀粒子の製造時に、必要に応じてアンモニア、チオエーテル、チオ尿素等の*

添加剤	RD-17643		RD-18716		RD-308119	
	頁	分類	頁	分類	頁	分類
化学増感剤	23	III	648	右上	996	III
増感色素	23	IV	648~649		996~8	IV
減感色素	23	IV			998	B
現像促進剤	29	XXI	648	右上		
カブリ抑制剤・安定剤						
	24	IV	649	右上	1006~7	VI
増白剤	24	V			998	V
硬膜剤	26	X	651	左	1004~5	X
界面活性剤	26~7	XI	650	右	1005~6	XI
帶電防止剤	27	XII	650	右	1006~7	XIII
可塑剤	27	XII	650	右	1006	XII
スベリ剤	27	XII				
マット剤	28	XVI	650	右	1008~9	XVI
バインダー	26	XXII			1003~4	IX
支持体	28	XVII			1009	XVII

本発明に係る感光材料に用いることのできる支持体としては、例えば前述のRD-17643の28頁及びRD-308119の1009頁に記載されているものが挙げられる。

【0130】適当な支持体としてはプラスチックフィルムなどで、これら支持体の表面は塗布層の接着をよくするために、下塗層を設けたり、コロナ放電、紫外線照射などを施してもよい。

【0131】

【実施例】以下、本発明を実施例にて説明するが、本発明は以下の実施例により限定されるものではない。

【0132】実施例1

1) 種乳剤の調製1

60°C、 $pAg=8$ 、 $pH=2.0$ にコントロールしつつ、ダブルジェット法で平均粒径0.2 μm の沃化銀 2モル%を含む沃化銀の単分散立法晶粒子を調製した。

44
* ハロゲン化銀溶剤を用いることができる。

【0127】乳剤は可溶性塩類を除去するためにヌードル水洗法、フロキュレーション沈降法などの水洗方法がなされてよい。好ましい水洗法としては、例えば特公昭35-16086号記載のスルホ基を含む芳香族炭化水素系アルデヒド樹脂を用いる方法、又は特開昭63-158644号記載の凝集高分子剤例示G3、G8などを用いる方法が特に好ましい脱塩法として挙げられる。

10 【0128】本発明に係る乳剤は、物理熟成又は化学熟成前後の工程において、各種の写真用添加剤を用いることができる。公知の添加剤としては例えばリサーチ・ディスクロージャーNo.17643(1978年12月)、同No.18716(1979年11月)及び同No.308119(1989年12月)に記載された化合物が挙げられる。これら三つのリサーチ・ディスクロージャーに示されている化合物種類と記載箇所を以下に掲載した。

【0129】

得られた反応液を40°Cにて花王アトラス社製、デモール水溶液と硫酸マグネシウム水溶液を用いて脱塩したのち、ゼラチン水溶液を加えて再分散し、種乳剤を得た。

2) 種乳剤からの成長1

40 上述の種乳剤を用い次のように粒子を成長させた。まず40°Cに保たれたゼラチン水溶液中に上記の種乳剤を分散し、さらにアンモニア水と酢酸でpHを9.7に調整した。この液にアンモニア性硝酸銀イオン水溶液及び臭化カリウムと沃化カリウムの水溶液をダブルジェット法で添加した。添加中は $pAg=7.3$ 、 pH を9.7に制御し沃化銀含有率35モル%の層を形成した。次にアンモニア性硝酸銀水溶液と臭化カリウム水溶液をダブルジェット法で添加した。目標粒径の95%までは $pAg=9.0$ に保ち、 pH は9.0~8.0にまで連続的に変化させた。その後 pAg を11.0に調整し pH を8.0に保ちながら目標粒径まで成長させた。続

いて酢酸でpHを6.0まで下げるから5,5'-ジクロロ-9-エチル-3,3'-ジ-(3-スルホプロピル)オキサカルボシアニンナトリウム塩の無水物をハロゲン化銀1モル当たり400mg添加し、前記のデモール水溶液と硫酸マグネシウム水溶液を用いて脱塩した後ゼラチン溶液を加えて再分散した。

【0133】この方法により平均沃化銀含有率2.0モル%の頂点が丸みを帯びた14面体で平均粒径0.35μm、0.40μm、0.65μm、変動係数がそれぞれ0.17、0.16、0.16の単分散沃化銀乳剤を(A)、(B)及び(C)を調製した。

【0134】乳剤の調製2

1) 種乳剤の調製2

30°Cで激しく攪拌した過酸化水素処理ゼラチンを含む0.05Nの臭化カリウム水溶液に、硝酸銀水溶液と過酸化水素処理ゼラチンを含む等モルの臭化カリウム水溶液をダブルジェット法で添加し、1.5分後から30分間かけて25°Cまで液温を下げるから硝酸銀1モル当たり80mlのアンモニア水(28%)を加え5分間攪拌を続けた。

【0135】その後、酢酸にてpHを6.0に合わせてからデモール水溶液と硫酸マグネシウム水溶液を用いて脱塩した後、ゼラチン水溶液を加えて再分散した。得られた種乳剤は平均粒径0.20μm、変動係数0.28の球型粒子だった。

【0136】2) 種乳剤からの成長2

上述の種乳剤を用い次のように粒子を成長させた。

【0137】75°Cで激しく攪拌したオセインゼラチンと、プロピレンオキシ-ポリエチレンオキシ-ジサクシネット-ジナトリウム塩を含む水溶液に臭化カリウムと沃化カリウムの水溶液及び硝酸銀水溶液をダブルジェット法で添加した。

【0138】この間pH=5.8、pAg=9.0に保った。添加*

1,1-ジメチロール-1-ブロム-1-ニトロメタン	70mg
t-ブチル-カテコール	400mg
ポリビニルビロリドン(分子量 10,000)	1.0mg
スチレン-無水マレイン酸共重合体	2.5g
ニトロフェニル-トリフェニルホスホニウムクロリド	50mg
2-アニリノ-4,6-ジメルカプトトリアジン	60mg
1,3-ジヒドロキシベンゼン-4-スルホン酸アンモニウム	4g
2-メルカプトベンツイミダゾール-5-スルホン酸ナトリウム	1.5mg
C ₄ H ₉ OCH ₂ CH(OH)CH ₂ N(CH ₂ COOH) ₂	1g
1-フェニル-5-メルカプトテトラゾール	15mg

【0143】

* 終了後pHを6.0に合わせ5,5'-ジクロロ-9-エチル-3,3'-ジ-(3-スルホプロピル)オキサカルボシアニンナトリウム塩の無水物をハロゲン化銀1モル当たり添加した。さらに40°Cにてデモール水溶液を用いて脱塩した後ゼラチン水溶液を加えて再分散した。

【0139】この方法により平均沃化銀含有率1.5モル%で投影面積直径0.76μm、変動係数0.25、アスペクト比が3.6の平板状沃化銀乳剤(D)を調製した。

【0140】試料の調製

10 得られた乳剤(A)、(B)、(C)及び(D)のそれぞれに、55°Cにて5,5'-ジクロロ-9-エチル-3,3'-ジ-(3-スルホプロピル)オキサカルボシアニンナトリウムの無水物と5,5'-ジ-(ブキシカルボニル)-1,1'-ジエチル-3,3'-ジ-(4-スルホブチル)ベンゾイミダゾロカルボシアニンナトリウム塩の無水物を200:1の重量比で、ハロゲン化銀1モル当たり(A)が975mg、(B)が600mg、(C)が390mg、(D)が500mg添加した。
10分後、適量に塩化金酸、チオ硫酸ナトリウム、チオシアノ酸アンモニウムを加えて化学熟成を行った。熟成20 終了15分前に沃化カリウムをハロゲン化銀1モル当たり200mg手添加し、その後4-ヒドロキシ-6-メチル-1,3,3a,7-テトラザインデンをハロゲン化銀1モル当たり3×10⁻²モル加え、ゼラチンを70g含む水溶液に分散した。
熟成済みの4種類の乳剤の内(A)は単独のまま乳剤Aとし、(B)と(C)は重量比で75:25の割合で混合し乳剤Bとし、(D)は単独のまま乳剤Cとした。

【0141】乳剤A、乳剤B及び乳剤Cのそれぞれに対し次の添加剤を加え感光性ハロゲン化銀乳剤塗布液とした。添加剤は以下の通りで、添加量はハロゲン化銀1モル当たりの量で示す。

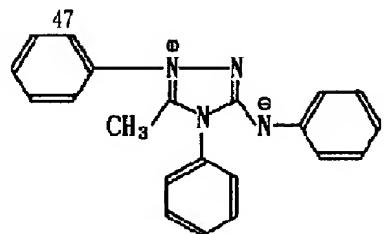
【0142】

【化29】

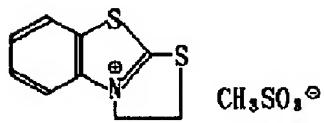
(25)

特開平5-257217

48



150mg



30mg

【0144】また保護層液に用いた添加剤は次の通りで * 【0145】

添加量は塗布液11当たりの量で示す。 *

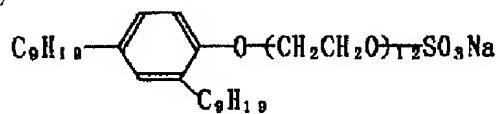
石灰処理イナートゼラチン	68g
酸処理ゼラチン	2g
ナトリウム-i-アミル- α -デシルスルホサクシネート	0.3g
ポリメチルメタクリレート(面積平均粒径3.5 μmのマット剤)	1.1g
二酸化ケイ素(面積平均粒径1.2 μmのマット剤)	0.5g
ルドックスAM(デュポン社製コロイダルシリカ)	30mg
2,2-ジクロロ-6-ヒドロキシ-1,3,5-トリアジンナトリウム塩 2%水溶液	10ml
グリオキザール40%水溶液 (CH ₂ =CHSO ₂ CH ₂) ₂ O	1.5ml 300mg

【0146】

【化30】

(26)

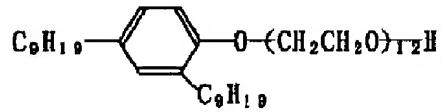
49



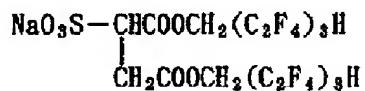
特開平5-257217

50

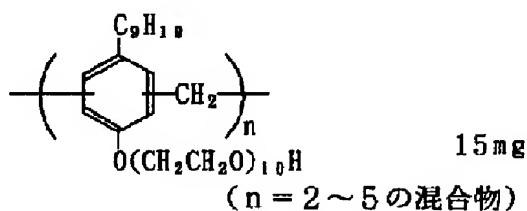
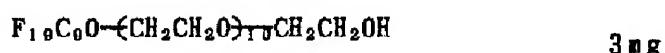
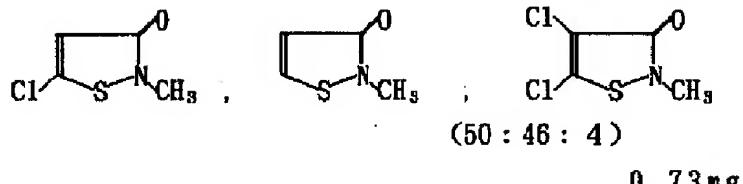
12mg



2mg



5mg



【0147】なお本発明に係る試料として、下記の表1のようにA面とB面の乳剤を構成して試料とした。

【0148】
【表1】

51

52

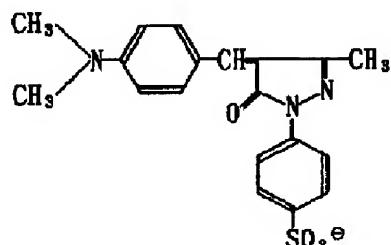
層構成 No.	A面			B面		
	乳剤	銀付量 (g/m ²)	最高濃度	乳剤	銀付量 (g/m ²)	最高濃度
I	B	3.65	3.45	—	—	—
II	B	1.8	1.73	B	1.8	1.73
III	B	1.8	1.73	A	1.5	1.75
IV	B	2.0	1.92	A	1.3	1.52
V	B	2.0	1.92	A	1.5	1.75
VI	C	1.8	2.01	A	1.3	1.77
VII	C	1.8	2.01	A	1.5	2.10
VIII	C	2.0	2.20	A	1.3	1.77

【0149】また、B面の乳剤上の保護層塗布液は、表2に示したように比較用パッキング染料（下記）及び本発明の染料銀塩を含む保護層塗布液を調製して塗布し

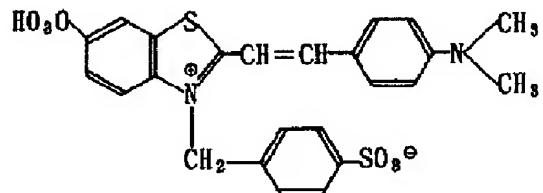
*た。

【0150】

*20 【化31】
パッキング染料（A）



パッキング染料（B）



【0151】性能の評価方法

写真性能

得られた試料フィルムの1~22について、P-45蛍光体使用のコニカイメージングカメラ タイプ-MM(コニカ〔株〕製)を用いてグレースケールで1/2秒露光した後、自動現像機SRX-502、現像液XD-SR、定着液XF-SR(いずれもコニカ〔株〕製)の指定処方を用い現像温度35℃、定着温度33℃、水洗水を18℃で毎分51を供給し、全

處理工程45秒モードで処理してセンシトメトリーカーブを得、相対感度とカブリを求めた。

【0152】また塗布したフィルムの1~22のB面側の感光層を蛋白分解酵素で除去することによってA面のみ濃度を求め、同様に試料からA面の感光層を除去することによってB面の濃度を測定した。これよりA面の濃度がカブリ+1.10になる露光量におけるB面の濃度DBを求めた。感度の値はカブリ+1.10の濃度を得るに必要な

輝度(Minolta TV Color Analyzer TV-2170, Probe No. 1 03054(ミノルタ〔株〕製)で測定した値の逆数として求め、試料No. 1を100としたときの相対感度で表した。

【0153】鮮鋭性

試料No. 1~19の画質の評価として鮮鋭性を SMPTE (Society of Motion Picture and Television Engineers 制定、日本医用画像工学会) 推奨のパターンを撮影し、高コントラストパターン、低コントラストパターンについて下記の基準により目視で解像度を評価した。

【0154】評価基準

- A : 1ピクセルまで識別できる
- B : 2ピクセルまで識別できる
- C : 3ピクセルまで識別できる
- D : 4ピクセルまで識別できる
- E : 5ピクセルまで識別できる

残色性の評価

染料色素に起因する残色性については、未露光の四つ切りサイズフィルムを自動現像機SRX-501、現像液XD-SR、定着液XF-SRを用いて35°C、45秒処理し処理フィルムを写真観察用光源台上で目視により評価した。

【0155】評価基準

- A : 色素残りが全くない

B : 色素残りは僅かにあるが、診断に支障がない

C : 色素残りが診断上気になる程度存在する

D : 色素残りが明らかに有り、診断上支障がある

残留銀の評価法

作成した前記の試料を未露光のまま上記と同様に45秒処理を行い残留銀評価用試料を作成した。残留銀の評価は次の方法で行った。

【0156】硫化ナトリウムの 2.6×10^{-3} mol/L水溶液を残留銀評価液として前記の残留銀評価フィルム上の5

10ヶ所に1滴ずつ滴下する。3分間放置後、液をよく拭きとて常温常湿下で15時間放置後、生成する硫化銀を写真濃度計PDA-65(コニカ〔株〕製)を用いて分光フィルター436±10nmの干渉フィルタで残留銀評価液滴下部分と滴下しない部分のブルー光透過濃度を測定し、その差を平均し残留銀量とした。

【0157】この差が大きい程処理後のフィルム中の残留銀濃度が高いことを示す。

【0158】本試験は、試料フィルムのA面とB面について行った。得られたこれらの結果を表2に示す。

20 【0159】

【表2】

試料 No.	フィル ム No.	染料		D B	写真性能			処理性		備 考
		例 示	添加量 (mg/m ²)		感度	カブリ	鮮鋭性	残色性	残留銀	
1	I	A+B	500	-	100	0.02	A	D	0.12	比較
2	II	-	-	0.25	95	0.02	E	A	0.02	"
3	III	A+B	500	0.03	80	0.02	B	C	0.02	"
4	III	1-2	500	0.03	96	0.01	A	A	0.02	本発明
5	IV	1-2	500	0.02	98	0.01	A	A	0.02	"
6	V	1-2	500	0.02	100	0.01	A	A	0.01	"
7	IV	1-5	500	0.02	99	0.01	A	A	0.01	"
8	IV	1-3	100	0.02	98	0.01	B	A	0.02	"
9	IV	1-3	300	0.02	97	0.01	A	A	0.01	"
10	IV	1-3	500	0.02	96	0.01	A	A	0.01	"
11	IV	2-1	800	0.02	97	0.01	A	B	0.02	"
12	IV	3-3	500	0.02	98	0.01	A	A	0.01	"
13	IV	5-3	500	0.02	98	0.01	A	A	0.02	"
14	IV	6-2	500	0.02	95	0.01	A	A	0.01	"
15	IV	8-1	500	0.02	97	0.01	A	A	0.01	"
16	IV	10-4	500	0.02	96	0.01	A	A	0.01	"
17	IV	6'-4	500	0.02	97	0.01	A	A	0.01	"
18	IV	9'-1	500	0.02	97	0.01	A	A	0.02	"
19	IV	11-4	500	0.02	98	0.01	A	A	0.02	"
20	VI	1-5	300	0.01	102	0.01	A	A	0.01	"
21	VII	1-5	300	0.01	102	0.01	A	A	0.01	"
22	VII	1-5	300	0.01	105	0.01	A	A	0.01	"

【0160】表2から明らかなように本発明の試料No.4~22は比較試料に比してカブリが少なく、かつ鮮鋭性が優れていた。また残色性、残留銀などによる現像処理後のフィルムの汚染要因の痕跡も認められなかった。

【0161】

【発明の効果】本発明により、迅速処理しても残色性、残留銀の発生がなく高感度、高鮮鋭性で高画質を有するC R T撮影用ハロゲン化銀写真感光材料を得られた。